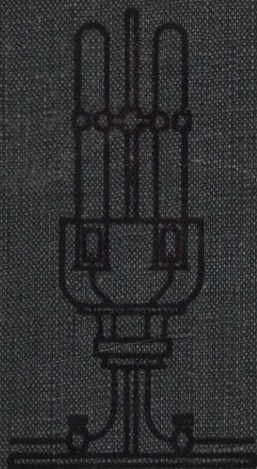
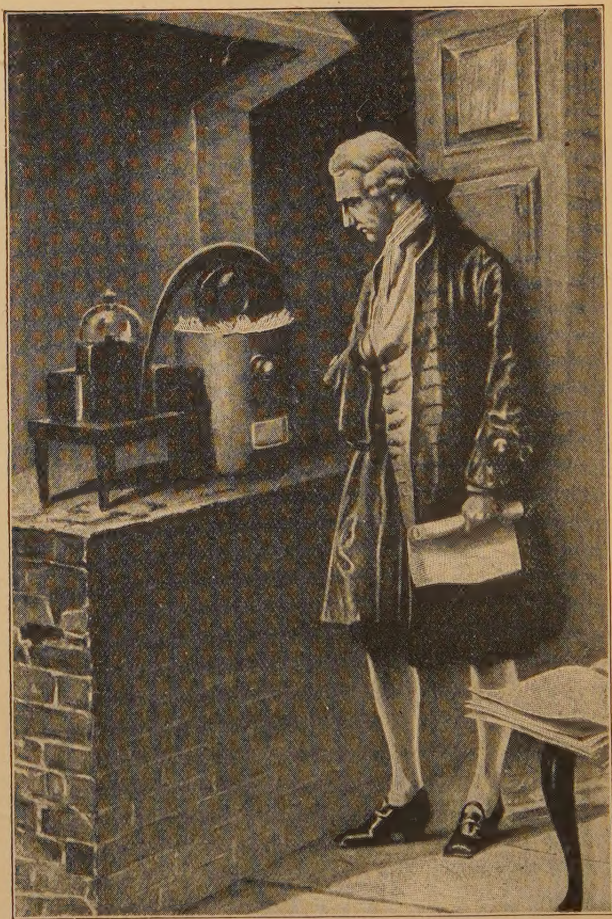


CHEMISTRY AND ITS USES



McPHERSON AND
HENDERSON



Lavoisier (1743-1794)

The great French chemist, Antoine Laurent Lavoisier, the founder of modern chemistry, is here shown in his laboratory conducting the famous experiments by which he proved the true nature of combustion. He was guillotined during the French Revolution because of his connection with the government

CHEMISTRY AND ITS USES

A TEXTBOOK FOR SECONDARY SCHOOLS

BY

WILLIAM McPHERSON

AND

WILLIAM EDWARDS HENDERSON



GINN AND COMPANY

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PREFACE

Every teacher of chemistry in the high school realizes that the watchword of the present day is the practical rather than the theoretical, the application rather than the abstract principle, the pictorial rather than the descriptive. Just how far this tendency should be followed each author and each teacher must decide for himself; this volume represents the opinion of the present authors. The text abounds in the practical applications of chemistry in the arts and industries as well as in everyday life, and no effort has been spared to have the illustrations as attractive, as instructive, and as accurate as possible. The authors have also kept before them the practical aim of presenting the occupation of the chemist as one that is very attractive to a boy who is thinking about what he will do in the world.

To the teachers using this book the authors wish to emphasize the conviction that the practical applications of chemistry have a place in high-school instruction largely in as far as they are used to illustrate the principles of the science and the way in which pure chemical knowledge can be turned to the uses of society. The main object of the course in chemistry must always be *to train young people to think and to imagine in the realm of chemical facts and laws*, and the teacher who finds at the end of the course that his pupil has acquired what seems to be a fund of useful information, but has little ability to think for himself how he would solve a simple chemical problem, should feel dissatisfied with his effort.

The utilization of chemical knowledge in the problems that developed during the World War is a fascinating story, and

many paragraphs have been devoted to this theme. It is hoped that the student will be led to see how chemistry can solve new problems when new conditions arise and will not rest content in merely contemplating the chemical triumphs of the war, great as these were.

Throughout the text a great many items of interesting information as well as supplementary explanation have been thrown into subordinate type. It is believed that the matter in large type is complete in itself and nowhere dependent on the subordinate paragraphs. However, it is thought that so much of interest will be found in these paragraphs that the teacher can easily induce the student to read them even if they are regarded as excess material. Directions for laboratory work will be found in a separate volume.

The authors are indebted to a large number of firms for assistance in securing photographs. Among these are the following: the Corning Glass Works, the American Rolling Mill Company, the Eastman Kodak Company, the Anaconda Copper Mining Company, the American Cyanamide Company, the H. V. Bretney Leather Company, the Goodrich Rubber Company, and the Koppers Company. Many high-school teachers have offered valued suggestions, and the authors desire to express their hearty appreciation to all these. We are especially indebted to our colleague, Mr. William Lloyd Evans, to Mr. George M. Strong, and to Mr. Robert W. Collins, instructors in chemistry in the East High School of Columbus, Ohio, and to Mr. Charles S. Pease and Mr. Julius Stone, Jr., of the Department of Chemistry, the Ohio State University. Mr. Strong and Mr. Stone not only read the proof but offered many suggestions as well.

THE AUTHORS

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CHEMISTRY AND ITS USES

CHAPTER I

CHEMISTRY AND THE WORK OF THE CHEMIST

The general field of chemistry. At the beginning of any new study it is well to get at least a general idea of the work ahead. So we may say at the outset of the course in chemistry that we shall be interested in the changes that the material things around us undergo. In some cases we notice that things change because they wear out or are broken, but they undergo no change in composition. Thus a dish may break and be valueless as a dish, but the pieces will have the same composition as the original dish. We shall have but little interest in such changes.

In most of the changes taking place around us it is evident that the very nature of the matter is changed. Thus, nearly all the metals tend to rust or corrode; coal and wood burn to form ashes and invisible gases; the constituents of the soil and the air are built up into a vast variety of living organisms; the food we eat is changed into fat and bone and muscle. In all these examples the materials undergo a change in composition, and it is in such changes that the chemist is especially interested. *The science of chemistry deals with all those changes that result in altering the composition of materials.*

Relation of chemistry to the other sciences. Since all the studies we call *natural sciences*, such as physics, biology, geology, and physical geography, in part deal with changes in the composition of materials, it is evident that chemistry is fundamental to all of them. We cannot study electrical

changes, or digestion, or rock disintegration without a knowledge of the exact changes that take place as well as of the general result of the changes. Physics and chemistry are really one science. Physics deals chiefly with what we call *energy*, — that is, with motion, heat, light, sound, electricity, — while chemistry deals with changes in the composition of *matter*. But almost every occurrence in nature that causes a change in matter causes a change in energy as well, and we cannot separate the two from each other. Moreover, the chemist is often interested quite as much in the energy set free when matter undergoes a change as in the change itself. For example, he is often called upon to measure the heat given off by burning a given sample of coal, for it is this that determines the value of the coal, and not the products that are formed.

The alchemists. In the earliest days of chemistry the chief chemical occupations were those of producing the metals from their ores, making glasses and enamels, and dyeing fabrics. There was no understanding of what happens in these processes, and the only guide was experience. In time the idea took a strong hold on the minds of these workers that the various metals are not really different things, but are merely stages in the purification of the one metal *gold*, and they thought that it ought to be possible to change all metals into gold in stages. These early chemists were called *alchemists*. It took centuries of work for them to become convinced that one metal cannot be changed into another. But in their efforts the alchemists found out many new facts, made many new compounds, and devised new processes, all of which had great practical value.

Almost at the time when the American Revolution for independence was starting, the great discovery of oxygen was made (1774), and the nature of the process we call *burning* or *combustion* became understood. This provided a sound foundation for the understanding of chemical processes of all kinds, and chemistry developed rapidly into a true science.

Nature supplies raw materials only. Very few of the materials found in nature are suited to the needs of man advanced beyond the most primitive stages of development. From the beginning he has had to match his wits against nature to gain materials better suited to his needs. At first he relied upon merely sorting out the best material and rejecting that of poor quality. For example, he pulled out the fine fibers from the stem of the flax plant, and he hammered or melted the small particles of gold found in sands into larger pieces. But he could not go very far in this way alone.

New materials from plants and animals. Man's most pressing need has always been for food and clothing. When natural species failed to supply his needs, he set about to improve on nature. The grains and vegetables and fruits we now grow for food and the plants that give us textile fibers bear little resemblance to the original plants of nature. The original beet had just enough sugar in it to suggest an idea; the modern beet has as much as 16 per cent. The cotton plant of nature would not be recognized beside the long-fibered plant of Arizona today. So, too, with the animals that supply us with meat, fat, milk, and wool. They have been very highly developed from primitive stock.

Very little of this work has been done by the chemist. Yet it must not be overlooked that each plant and animal is doing just what the chemist does in his laboratory. It takes the raw materials supplied by nature and builds them up by chemical changes into very diversified products. *All living organisms are therefore chemical laboratories*—much more wonderful and efficient than the ones we build. So in improving a plant or animal we are really improving a chemical process.

New materials from inanimate products. The chemist for the most part works with matter that is not living; namely, with the minerals supplied by nature and with the products of life such as fats, oils, sugars, starch, and hundreds of similar products.

From these he has developed countless new materials for human needs. From the rocks he has prepared a large array of useful metals and such indispensable things as lime and cement. From coal he has manufactured thousands of dyes, medicinal preparations, fertilizers, paints, and other useful but less familiar materials. From petroleum and wood and the saps of trees, from milk and hides and hoofs, he has fashioned the materials that make the physical comforts surrounding the lives of even the poorest luxurious when compared with the possessions of the kings of the past.

Chemical industries. All the industries that transform a raw material of nature into a finished product for human use are essentially chemical industries. They must rest on the principles of chemical science, and they must be supervised by someone who understands chemistry. It is only as our knowledge of chemistry increases that these industries can be conducted more economically and expanded into more efficient and diversified ones. *The industrial advancement of a country can be judged fairly well by the extent to which chemistry is cultivated in its schools and universities.*

The work of the chemist. Some chemists will always be chiefly interested in adding to our knowledge of chemistry as a science. Others will have as their greatest interest some definite industrial plant (Fig. 4). Such a one must supervise the process used in the industry and devise improvements. He must find out the composition of each new lot of raw material and modify the process accordingly. He must be able to guarantee the composition and the properties of the output of the factory so that its value may be known. He must study the possibilities of making something useful out of the waste products of the business. For example, he has taken the formerly useless cotton seed and from it has made most valuable oils, fats, soaps, and cattle feeds. Since industry has such a wide range of raw materials employed, there is almost no limit to

FIG. 1. Ira Remsen
(1846-)

For many years director of chemical research at the Johns Hopkins University, later president of that institution; known equally well as a great chemist, an inspiring teacher, and an educational leader; editor of an important chemical journal and the author of an important series of books; president of the American Chemical Society (1902); member and officer in many of the important scientific societies of this country as well as foreign member of many European societies



FIG. 2. Edgar Fahs Smith
(1856-)

For many years director of chemical research at the University of Pennsylvania and later president of that institution; noted for his contributions to electrochemistry and to our knowledge of the rarer elements; a writer of fascinating interest on the early history of chemistry in the United States; president of the American Chemical Society (1895, 1921, and 1922); member and officer in many scientific societies in this country and abroad





FIG. 3. An alchemist in his laboratory.



FIG. 4. A typical laboratory of a modern automobile plant

the variety of the work of the chemist. The chemist also helps to preserve the health of the people by finding out the kinds and amounts of food best adapted to our bodies, by devising methods for purifying our water supplies and for disposing of sewage, and by preparing various substances that are useful in combating diseases.

Chemical knowledge incomplete. While we seem to know a good deal about changes in matter, we have really just made a good beginning. For example, our knowledge of what takes place in growing plants and animals is very limited, though we are learning fast. Plants manufacture sugar and starch and cellulose chiefly from air and water, but we cannot do this in the most expensively equipped laboratories, nor do we understand how the commonest plant accomplishes this seeming miracle. Even in well-understood processes there is usually some detail that is not yet clear.

The future of chemistry. There is a wealth of unsolved problems of vast importance to human comfort and happiness to attract the student to the life pursuit of chemistry. For example, we are rapidly using up our reserves of easily available raw materials, such as coal, oil, gas, wood, and metal ores, and substitutes must be found. We are exhausting our fertile lands, and we must learn better how to keep them in productive condition. Every line of material progress along which we are moving is full of these problems, and as a result the number of those engaged in chemical occupations is increasing very fast. In every progressive country the national chemical society is one of the largest of the scientific organizations. The American Chemical Society is the largest scientific society in the world, having more than 15,000 members.

CHAPTER II

MATTER AND ITS CLASSIFICATION

Definition of matter. Since the chemist is interested primarily in matter and the changes it undergoes, it is important for us to get a clear idea of just what we mean by matter. For our purposes we may define matter *as anything that has weight or occupies space*. This not only includes solid and liquid materials that we can see and touch but also the various gases, such as those that make up the atmosphere and which, although invisible, are very real and fit the definition of matter just given.

Classification of matter. From the standpoint of its physical state it is customary to classify matter under three headings: namely, *solids*, *liquids*, and *gases*. The chemist, however, is interested in matter from the standpoint of its composition, and from this standpoint it may be classified under two headings: *elements* and *compounds*.

Elements. As we proceed with our study we shall find that there exists a relatively small number of simple forms of matter and that all other forms of matter are built up by the union of two or more of these simpler forms. *These simple forms of matter are called elementary substances or, more briefly, elements*. Many of them, such as iron, copper, oxygen, gold, are well known to us. Chemists have good reason for believing that ninety-two such elements exist. Of these, eighty-seven are now known, leaving five to be discovered. A complete list of the known elements is given on the page opposite the back cover.

Most of the elements are solids. Of the known elements ten are gases, while only two — namely, mercury and bromine — are liquids under ordinary conditions.

Compounds. While the number of elements is comparatively small (ninety-two in all), there are, on the other hand, many thousands of substances that are made up of two or more elements. Thus, if a current of electricity is passed through water (Fig. 9), the water is decomposed into two elements (both of which are invisible gases), known respectively as *oxygen* and *hydrogen*. Again, the ordinary iron ore known as hematite can be shown to consist of the two elements iron and oxygen. The sugar with which we sweeten our food is composed of the three elements carbon, hydrogen, and oxygen. Such substances as water, iron ore, and sugar are known as *compounds*. *Compounds, however, are not only made up of two or more elements, but each compound has a perfectly definite composition.* For example, we shall see later that water is made up of hydrogen and oxygen in the ratio of one part by weight of hydrogen to 7.94 parts by weight of oxygen. It makes no difference what the source of the water is, provided only that it is pure; the composition is always the same. This constancy of composition is characteristic of all compounds. We may therefore define a compound as *a substance made up of two or more elements combined in definite proportions by weight.*

Illustration. We might, in a very general way, compare the elements to the letters of the alphabet. Just as the printed matter on this page is made up of single letters and of combinations of letters to form words, so matter is made up of elements and of combinations of elements in the form of compounds. Just as there are a great many more words than letters, so there are a great many more compounds than elements.

Chemical changes — chemical action. We may best illustrate the meaning of these terms by a simple illustration. If we place in a test tube one or two grams of the red solid substance known as *mercuric oxide* and heat it (Fig. 5), we find that the color gradually changes and that there is left in the tube little drops of a silverlike liquid which we recognize as *mercury*,

or quicksilver, as it is often called, which is used in thermometers and barometers. If during the heating we thrust into the mouth of the tube a glowing splint, the wood will burst into a flame. Experiments show that this bursting into flame is due to the presence of the invisible gas, *oxygen*, which is evolved on heating

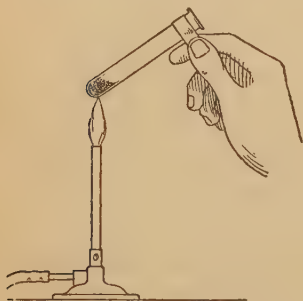


FIG. 5. The decomposition of mercuric oxide into mercury and oxygen by heat

the mercuric oxide. The red solid, mercuric oxide, then has been decomposed by the heat into two elements, the one a silverlike liquid and the other an invisible gas. A change like this is known as a *chemical change*, and in describing it we say that *chemical action* has taken place. Such changes are taking place all about us, and they are the ones in which the chemist is particularly interested. Thus, coal and wood burn, being changed

in the process into ashes and invisible gases. The food we eat is changed into the tissues of the body. *In all such changes the substances resulting from the chemical action differ in composition from the substances originally present and usually differ from them in appearance as well.* We shall see later on that there are other important changes which always accompany chemical action. *At present, for our purposes, we may define a chemical change as one that is attended by a change in the composition of matter.*

Changes that are not attended by a change in the composition of matter, such as the breaking of a piece of glass or the powdering of a lump of coal, are known as *physical changes*.

It follows from the statements made above that the appearance of a compound gives no clue as to what elements are present in it. Thus the red solid, mercuric oxide, is formed by the union of the silverlike liquid, mercury, with the invisible

gas, oxygen. Water, a colorless liquid, is formed by the union of two invisible gases, oxygen and hydrogen. No one would ever suspect simply from appearance that sugar contains the black solid element carbon, and yet if we heat sugar the hydrogen and oxygen with which the carbon is combined in the sugar are expelled and the black carbon remains.

Chemical affinity. *The force that causes elements to unite and holds them in combination in compounds is called chemical affinity.* We know very little about the nature of this force, just as we know very little about the force of gravitation. It is evident, however, that there is such a force, and it is convenient to have a name by which we can refer to it.

Relative abundance of the elements. Many of the elements, such as oxygen and iron, are very abundant. Many others are rare, and in some cases not more than a few grains have been obtained pure. Clarke makes the following estimate of the composition of the solid portion of the earth's crust:

COMPOSITION OF THE EARTH'S CRUST

Oxygen . O	47.33%	Magnesium . Mg	2.24%
Silicon . Si	27.74%	Sodium . Na	2.46%
Aluminium . Al	7.85%	Potassium . K	2.46%
Iron . . Fe	4.50%	Hydrogen . H	0.22%
Calcium . Ca	3.47%	Other elements	1.73%

It is not necessary to study more than one third of the total number of elements to gain a very good knowledge of chemistry. The more common elements are printed in heavy type in the table of elements given on the page opposite the back cover.

4. **Elements in the human body.** Comparatively few of the elements appear to be essential to life. The following table, compiled by Sherman, gives the average composition of the human body. So far as we can judge, these are the only ones upon which living organisms are dependent, though traces of others may be necessary.

AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen . . .	65.00%	Phosphorus . . .	1.00%	Magnesium . . .	0.05%
Carbon . . .	18.00%	Potassium . . .	0.35%	Iron . . .	0.004%
Hydrogen . . .	10.00%	Sulfur . . .	0.25%	Iodine . . .	traces
Nitrogen . . .	3.00%	Sodium . . .	0.15%	Fluorine . . .	traces
Calcium . . .	2.00%	Chlorine . . .	0.15%	Silicon . . .	traces

Occurrence of the elements. Most of the elements occur in nature not as uncombined substances but in the form of chemical compounds. When an element does occur uncombined, as is the case with gold and sulfur, we say that it occurs *in the free state*, or *native*; when it is combined with other substances in the form of compounds, we say that it occurs *in the combined state*, or *in combination*. The elements present in our bodies are all in the form of compounds, of which water is the most abundant.

Names of elements. The names given to the elements have been selected in a great many different ways. Some names, such as iron and gold, are very old, and their original meaning is obscure. Many names indicate some striking property of the element. The name *bromine*, for example, means "stench," referring to the extremely unpleasant odor of the substance. Other elements are named from countries or localities, as germanium and scandium. Still others are named from some mythological character, as thorium and tantalum.

Symbols. In indicating the elements chemists have adopted a system of abbreviations. These are known as *symbols*, each element having a distinctive symbol. Sometimes the initial letter of the name is adopted to indicate the element. Thus, I stands for iodine, C for carbon. Usually it is necessary to add some other characteristic letter to the symbol, since several names may begin with the same letter. Thus, C stands for carbon, Cl for chlorine, Cd for cadmium. Sometimes the symbol is an abbreviation of the name in some other language.

In this way Fe (Latin, *ferrum*) indicates iron, Cu (Latin, *cuprum*) indicates copper, and Ag (Latin, *argentum*) indicates silver. The symbols will be found in the list of elements given on the back cover page. They will become familiar through constant use.

The number of compounds. The number of compounds which have been described and which can be made when desired is very large, and each year many more are added to the list. About 200,000 are known that contain the element carbon as one constituent, and the total number listed in the large handbooks of chemistry is much larger. Fortunately it is not necessary to become familiar with any large number of these in order to gain an understanding of the principles of chemistry.

Meaning of the terms *mixture* and *substance*. We have discussed the nature of elements and compounds and learned something of their characteristics. It is possible for us to mix intimately together many different elements and compounds without any chemical action taking place. The resulting product is called a *mixture*. Thus, we may have a mixture of sand and salt or of sugar and flour. Such products differ from compounds in that their composition may be varied indefinitely; moreover, in a typical mixture particles of different character may be distinguished, while in a compound all particles, no matter how minute, are identical in composition and properties. When we wish to refer to some form of matter without regard to its composition, we often use the term *substance*. Thus, we might speak of an element, a compound, or a mixture as a substance.

Method of study. We shall now proceed with a study of some of the more important elements. As a rule each element will be discussed under the following heads: (1) *Properties*. By this word is meant all those physical characteristics of a substance by which we recognize it. This includes its state (solid, liquid, or gas), color, odor, and taste. It also

includes certain measured quantities such as weight, hardness, solubility, boiling point, freezing point. (2) *Occurrence in nature*. Under this heading will be discussed such topics as the forms in which the element occurs in nature, whether free or in the combined state, whether it is an abundant element or of rare occurrence. (3) *Historical study*. It is always of interest to know something concerning the discovery of the element and other items of historical interest in connection with it. (4) *Preparation*. As a rule the elements do not occur pure in nature but are mixed or combined with various other substances. It becomes necessary, therefore, to find out methods whereby the elements can be separated from other substances and thus obtained in a pure state. (5) *Chemical conduct*. Under this head will be described the various chemical changes in which the element plays a part and the methods for producing these changes. In studying oxygen, for example, we shall want to know what other elements will combine with oxygen, the conditions necessary to bring about the combination, and the nature of the resulting products. (6) *Uses*. From a practical standpoint it is important for us to learn of the various uses to which the different elements are adapted.

Method of recording temperatures. Unless otherwise indicated, all temperatures given in this book refer to the centigrade system. Any student not familiar with the centigrade system of recording temperatures will find a brief explanation of it in the Appendix.

EXERCISES

1. What means have been mentioned for decomposing a compound?
2. Define the following terms and give an example to illustrate each: (a) matter, (b) element, (c) compound, (d) mixture.
3. Define the terms (a) chemical change, (b) chemical affinity.
4. Does the fact that a substance undergoes no change on heating prove it to be an element?

5. Read over the list of elements. (*a*) With what ones are you familiar? (*b*) Is brass an element?

6. Taking into account possible future discoveries, in what way may the list of elements (see Appendix) be changed?

7. How do you account for the fact that the Ancients were familiar with copper and gold?

8. Give three examples of chemical changes with which you are familiar.

9. Can you tell from the appearance of a compound whether or not it contains iron?

10. If a substance such as a candle disappears on burning, does this prove that the matter in it is destroyed?

11. Calculate approximately the number of pounds of the more important elements present in your body.

12. (*a*) What is the approximate weight of iron in your body? (*b*) Does the fact that the amount of iron is so small signify that it is unnecessary?

13. In round numbers, what part of the world is oxygen?

14. Aluminium is much more abundant than iron. How do you account for the fact that iron is much the cheaper of the two metals?

15. Compare the relative quantities of iron and silicon in the earth's crust. How do you account for the fact that everyone is familiar with iron and but very few with silicon?

16. Consult the dictionary for the derivation and significance of the following names of elements: (*a*) phosphorus, (*b*) hydrogen, (*c*) germanium, (*d*) columbium, (*e*) chlorine, (*f*) argon, (*g*) copper, (*h*) selenium, (*i*) thorium, (*j*) tantalum.

17. (*a*) What is the symbol for gold? (*b*) From what word is this symbol derived? (Consult dictionary.)

18. Give some typical examples of mixtures.

19. How can you tell whether any given substance is a mixture or a compound?

20. Common alcohol boils at 78.3°C . At what temperature does it boil on the Fahrenheit scale?

21. Mercury freezes at -38.87°C . Calculate the corresponding Fahrenheit temperature.

CHAPTER III

OXYGEN

Introduction. Having become acquainted with a few of the characteristics of the class of substances called elements, we shall now turn to a more detailed study of two members of this class; namely, oxygen and hydrogen. It is natural that we should begin with oxygen, since it is the most abundant of all elements, occurs in nature in great quantities in the elementary state, and plays such an important part in the familiar processes of burning and breathing.

Properties of oxygen. Oxygen is one of the gases present in the atmosphere and is of fundamental importance, since it is the one which supports life. It is a colorless, tasteless, and odorless gas and is slightly heavier than air. One liter of oxygen weighs 1.429 g., while 1 liter of air weighs 1.2928 g. It is but slightly soluble in water, 100 volumes of water dissolving only about 4 volumes of the gas at ordinary temperatures and pressures.

It is well known that gases expand on heating, also that the quantity of gas that occupies a certain volume (say, that of a given automobile tire) may be greatly increased by pressure. It is evident, therefore, that the weight of (say) 1 liter of a gas will vary with the temperature of the gas and the pressure to which it is subjected when weighed. We shall find later that in making such a statement as "1 liter of oxygen weighs 1.429 g." it is understood that this is the weight of 1 liter of oxygen measured at 0° and a pressure of 1 atmosphere; that is, 1033 g. per square centimeter.

Occurrence. Oxygen is by far the most abundant of the elements. In the free state it forms a considerable part of the

atmosphere. One hundred volumes of *dry* air contains about 21 volumes of oxygen mixed with 78 volumes of the gas *nitrogen* and 1 volume of other gases. Combined with other elements, oxygen forms eight ninths by weight of water, nearly one half of the rocks constituting the earth's crust, and over one half of animal and vegetable organisms; for example, 65 per cent by weight of the human body is oxygen.

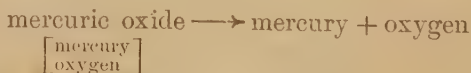
Historical. The Englishman Joseph Priestley (Fig. 6) is commonly regarded as the discoverer of oxygen, although other investigators, especially the Swedish chemist Scheele, had obtained it before Priestley, but had failed to attract attention to their discovery. The name *orygen* signifies "acid producer." It was suggested by the French chemist Lavoisier (frontispiece) because he thought that the class of substances known as acids owe their characteristic properties to the presence in them of this element. We now know that Lavoisier was mistaken in this view, for there are many acids that contain no oxygen.

Priestley was born near Leeds, England, in 1733. He was educated for the ministry, but became interested in science and spent much of his spare time in performing experiments. In 1774, while studying gases, or "airs," as he called them, he heated the compound now known as mercuric oxide by means of a large burning-glass and found that a colorless gas was evolved. This gas, which Lavoisier later named oxygen, attracted his attention because a candle burned in it with a brilliant flame. Later Priestley had to leave England because of his liberal views. He came to America in 1794 and settled in Northumberland, Pennsylvania, where he resided until his death in 1804. The house in which he lived still stands and is preserved as a memorial to him.

Preparation. While oxygen is the most abundant of all the elements it does not occur in nature in a pure state, but always either mixed with other gases, as in the air, or combined with other elements in the form of compounds. Since it is so

abundant in the air one would naturally try to obtain it from this source. The separation of the oxygen from the other gases present in the air, however, is a difficult matter, requiring expensive machinery, and is only practicable when large volumes of the gas are desired. In the laboratory, where only small amounts are wanted for a study of the properties of the element, it is most conveniently prepared by decomposing certain of its compounds, either by heat or electricity, and collecting the oxygen evolved. The compounds usually employed are (1) mercuric oxide, (2) potassium chlorate, and (3) water.

1. *Preparation from mercuric oxide.* Mercuric oxide is a solid, either red or yellow (depending on its method of preparation), and consists of 7.4 per cent oxygen and 92.6 per cent mercury. If a small quantity of this oxide is placed in a narrow test tube and heated (Fig. 5), it is readily decomposed into its constituent elements. The change may be represented in the following way, in which the names of the elements composing the compound are inclosed in brackets just beneath the name of the compound:



The mercury is seen to deposit on the sides of the tube, while the presence of oxygen is shown by the fact that a glowing spark on the end of a splinter of wood inserted into the tube bursts into a bright flame. This method is too expensive for ordinary use, but it is of interest because of its simplicity and because it is the one which Priestley used in preparing oxygen.

2. *Preparation from potassium chlorate (usual laboratory method).* Potassium chlorate is a white solid which has been found to consist of 31.9 per cent potassium, 28.9 per cent chlorine, and 39.2 per cent oxygen. When this compound is

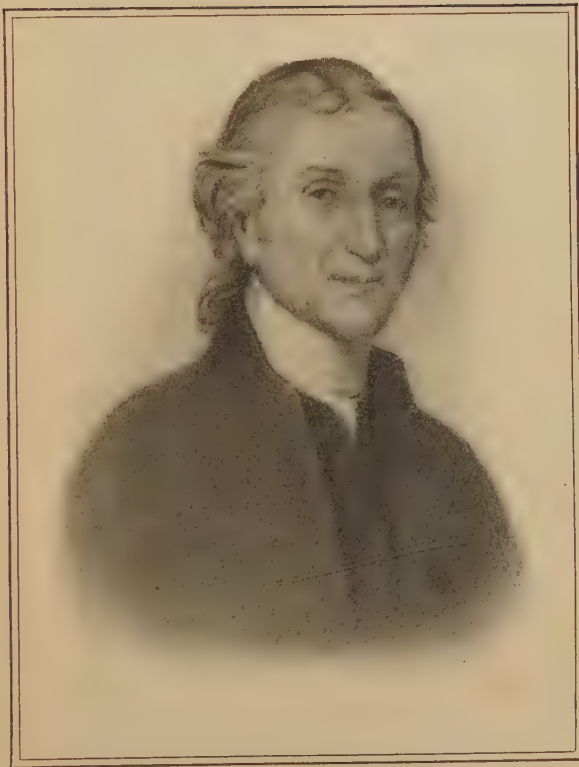


FIG. 6. Joseph Priestley (1733-1804)

School-teacher, preacher, philosopher, scientist; friend of Benjamin Franklin; discoverer of oxygen; defender of the phlogiston theory. He was born in England, where he lived until he was sixty-one years of age; he then came to the United States and spent the remainder of his life at Northumberland, Pennsylvania

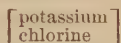
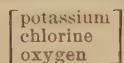


FIG. 7. View of the *R-34* as she lay at Mineola, New York, July 7, 1919

The *R-34* (the first dirigible to cross the ocean) was 613 ft. in length and was constructed largely of aluminum, a strong light metal. This photograph shows the preparations for the return flight of 3200 miles to England. The journey was completed in seventy-five hours and three minutes. The *R-34* was inflated with 2,000,000 cu. ft. of hydrogen, the lightest of all gases. The rows of iron cylinders shown here contained the hydrogen used in inflating the dirigible

heated above its melting point the oxygen is given off, leaving a white solid compound of potassium and chlorine called potassium chloride. The change may be represented as follows:

potassium chlorate $\longrightarrow$ potassium chloride + oxygen



The evolution of the gas becomes marked at about 400°. It is a remarkable fact that the rate at which the oxygen is evolved at any given temperature is greatly increased by the presence of small quantities of certain substances, notably manganese dioxide. By mixing such a substance with the chlorate it is possible, therefore, to obtain the oxygen rapidly at a lower temperature than would otherwise have to be employed. As to the way in which the manganese dioxide promotes the decomposition, it may be said at once that we do not know. Apparently it undergoes no change during the reaction. Certainly it contributes no oxygen, for the weight of oxygen obtained is always 39.2 per cent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. *This is but one example of many in which the rate of change is influenced by an apparently inactive substance.* Such substances are called *catalytic agents*, or *catalyzers*, and we shall meet with them frequently in subsequent pages, since a great many chemical processes depend upon suitable catalyzers for their success.

Directions for preparing oxygen. A convenient way of preparing oxygen from potassium chlorate is illustrated in the diagram (Fig. 8) on page 18. A mixture consisting of four parts of potassium chlorate and one part of manganese dioxide is placed in the flask *A* and gently heated. The oxygen is evolved and escapes through the tube *B*. It is collected by bringing over the end of the delivery tube the mouth of a bottle or cylinder *C* completely filled with water and inverted in a vessel of water as shown in the figure. The gas rises in the bottle and displaces the water.

Collection of gases. The method just described for collecting oxygen illustrates the general way in which gases are transferred from one vessel to another when they are insoluble in water or nearly so. The vessel *D* (Fig. 8), containing the water in which the bottles are inverted, is called a *pneumatic trough*.

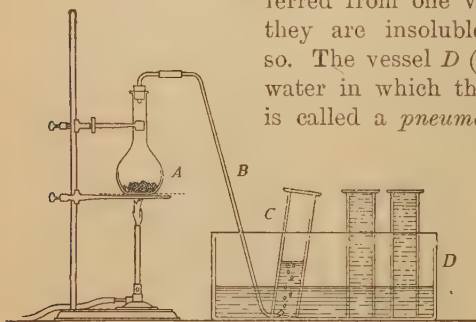


FIG. 8. Preparation of oxygen from potassium chlorate, and method of collecting the gas

3. Preparation from water. As we shall later see, water is a compound and contains 88.81 per cent oxygen and 11.19 per cent hydrogen. It is not practicable to de-

compose it into its elements by heat, but the decomposition is easily effected by the use of electrical energy in the following way:

Two tubes, *A* and *B* (Fig. 9), are filled with water and inverted in a vessel of water to which a little sulfuric acid has been added. A piece of platinum foil, *C* and *D*, attached to a wire is then brought under the end of each tube. When these wires are connected with a suitable source of current, supplying from 6 to 10 volts, bubbles of gas collect in each tube. These gases are oxygen and hydrogen. The volume of the hydrogen (tube *A*) liberated is approximately twice that of the oxygen (tube *B*). The reasons for adding sulfuric acid will be explained later on.

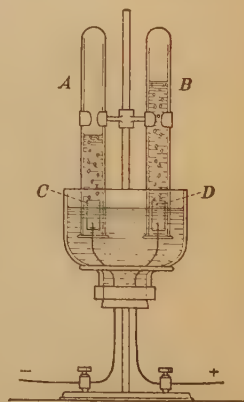


FIG. 9. The decomposition of water into oxygen and hydrogen by the electric current

The change which takes place when a current of electricity is passed through a liquid is called electrolysis. In the above experiment the oxygen is said to be obtained by the electrolysis of water.

Commercial preparation of oxygen. Oxygen is now a common article of commerce and can be purchased on the market, stored in strong steel cylinders (Fig. 10). When wanted in large quantities it is prepared almost entirely from air. The method used will be described later.

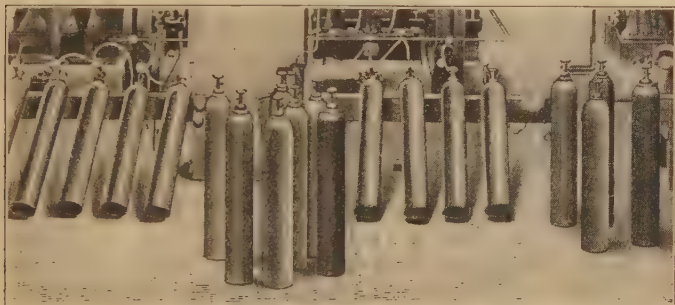


FIG. 10. Oxygen stored in steel cylinders, ready for the market

Laboratory methods and commercial methods. As we go along we shall see that the methods used in making various substances in the laboratory are often different from those employed commercially. In the laboratory, where relatively small quantities are desired, the easiest or most instructive way is preferred. In commerce economy is the deciding factor. Moreover, it often happens that a method which will not work well on a small scale works admirably with commercial quantities, or that the value of a second product (*by-product*) obtained at the same time makes a method a success.

Chemical conduct. At ordinary temperatures oxygen is not very active. Most substances are either not affected by it or the action is so slow as to escape notice. At higher temperatures, however, it is very active. This may be shown by heating various substances in the air until just ignited and then bringing them into vessels containing pure oxygen, when they burn with increased brilliancy. Thus a glowing splint introduced into a bottle of pure oxygen bursts into flame.

Sulfur burns in air with a very little flame; in oxygen the flame is increased in size and brilliancy (Fig. 11). Substances which burn in air only with great difficulty, such as iron, burn readily in oxygen; while others, such as phosphorus, which burn readily in air, burn in oxygen with dazzling brilliancy.

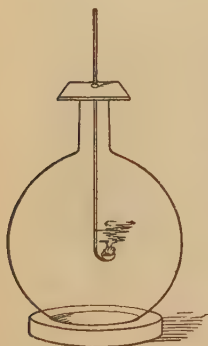


FIG. 11. Burning sulfur in oxygen

Changes which take place in burning.

Since burning is such a common phenomenon it has long attracted attention, and there has been much speculation not only as to the changes which take place in burning but also as to why certain substances burn and others do not. For some time previous to the discovery of oxygen it was thought that all substances which burn contain in them an invisible material called *phlogiston* and that the burning of a substance was due to the escape of phlogiston present. After Priestley discovered oxygen Lavoisier concluded that since substances burn so readily in oxygen this gas must have something to do with burning. This view would satisfactorily account for the fact that substances burn more readily in pure oxygen than in the air, which is only about one fifth oxygen. In place of merely speculating about it Lavoisier put his views to the test of experiments (frontispiece), which is the only way to find out the facts. He soon found that metals when burned in a vessel filled with air or oxygen increase in weight and that at the same time a certain amount of the oxygen present disappears. Moreover, he found that the increase in the weight of the metal in burning was equal to the weight of the oxygen which disappeared. He therefore came to the conclusion that *when a metal or, indeed, any element burns it combines with oxygen, and that the product formed is a compound of the element and oxygen.* This discovery of Lavoisier,

which led to the true explanation of burning, is regarded as one of the greatest of all discoveries made in the field of chemistry.

Not only do many of the elements burn in oxygen, but many compounds also burn in this gas. In such cases, as a rule, the compound is decomposed, and each of its constituent elements combines with the oxygen.

Disappearance of some substances in burning. When some substances, such as a candle, burn they entirely disappear, and it might appear at first thought that this is not in accord with Lavoisier's explanation. A little reflection, however, might suggest that such substances disappear in burning because the compounds formed on burning are invisible gases which pass off unnoticed into the air. That this is the case and that these gases weigh more than the original candle is easily shown in the following way:

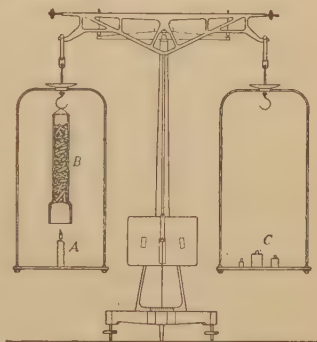


FIG. 12. Experiment to show that invisible gases are formed when a candle burns and that these gases weigh more than the burned part of the candle

A candle (A) is placed on one pan of a balance (Fig. 12). Over it is suspended a wide glass tube (B) loosely filled with pieces of quicklime or caustic potash. The whole apparatus is carefully counterpoised by weights (C); then the candle is lighted. As the candle burns, the pan upon which it rests gradually sinks, indicating that the gases formed during burning and absorbed in the tube over the flame are heavier than the part of the candle which has burned. We shall find later that the gases formed in the burning of the candle are the compounds known as carbon dioxide and water. The glass tube is filled with quicklime, because this substance readily absorbs both these gases.

Oxidation ; combustion. When a substance combines with oxygen we say that the substance undergoes *oxidation*. If the

change takes place slowly no light is evolved, and unless careful measurements are made no heat is noticed. The decay of vegetable matter such as wood and leaves and the rusting of certain metals are examples of this slow oxidation. If, on the other hand, the process takes place rapidly, light is given off, and we say that the substance burns or undergoes *combustion*. These statements may be summed up as follows: *Oxidation is the term applied to the change which takes place when a substance combines with oxygen. Oxidation which takes place so rapidly as to evolve light is called combustion.*

The term *combustion* as commonly used implies that oxygen is one of the substances entering into the change. This is always the case when a substance undergoes combustion in air. In a broader sense, however, the term is often applied to the change which takes place when any two substances combine with the evolution of light.

Oxides ; products of combustion. We have seen that when an element burns there is formed a compound of the element with oxygen. Such compounds are called *oxides*. Thus, iron on burning forms oxide of iron, and sulfur forms oxide of sulfur. A candle is composed chiefly of carbon and hydrogen. When it burns the carbon unites with oxygen to form oxide of carbon, while the hydrogen unites with oxygen to form water, which is an oxide of hydrogen. All but about half a dozen elements form oxides, and many of them form more than one, so that a large number of these compounds is known. Some of these are solid bodies, as in the case of oxides of mercury and iron ; others are liquids, of which class water is the most familiar example ; quite a number are gases, as is true of the oxides of carbon and of sulfur.

The oxides formed when any substance undergoes combustion are known as the *products of combustion* of that substance. Thus, oxide of iron is the product of combustion of iron, while carbon dioxide and water are the products of combustion of the candle.

To sum up these facts we may say then that *an oxide is a compound formed by the union of any one element with oxygen. The particular oxides formed when a substance undergoes combustion are known as the products of combustion of that substance.*

Rapidity (or speed) of combustion. It is a matter of common knowledge that the same substance may burn with different degrees of rapidity, and it is important for us to know how the rapidity, or speed, of the combustion can be increased or decreased. A number of factors may affect this change of speed, but the two most important are the following:

1. **Temperature.** Everyone knows that a lump of coal if ignited and placed on a piece of hot iron will burn more rapidly than a similar one placed on a piece of cold iron. This is due to the fact that the hot iron rapidly increases the temperature of the coal, and this increase in temperature causes a corresponding increase in combustion. Within certain limits it may be stated in general terms *that combustion takes place more rapidly the higher the temperature.* Oxidations which may require years for completion at a low temperature may take place in a few seconds at a very high temperature.

2. **Concentration.** Since ordinary combustion is due to the union of one or more elements with oxygen, it follows that the more oxygen that can be brought into contact with the substance undergoing combustion, the more rapidly the combination may take place. Thus a log of wood burns slowly. Cut the log into pieces, and the speed of combustion increases because more oxygen comes in contact with the wood. Split the pieces into fine splinters and the speed of combustion is still further increased. Grind the splinters into fine dust and float these in the air so that each little particle is surrounded by the oxygen in the air, and combustion, if started, will take place so rapidly as to be nearly instantaneous, producing a violent explosion. In this way we account for the explosions of

flour mills and grain elevators, the air of which often contains large quantities of dust particles (Fig. 13).

Heat of oxidation and combustion. Evidently a given substance may either undergo a slow oxidation or it may undergo combustion. Thus a piece of phosphorus exposed to the air in a cold room slowly wastes away until it has all disappeared



FIG. 13. That a mixture of air and dust may explode violently is shown by the above picture of a flour mill in Beatrice, Nebraska, taken just after a dust explosion had occurred

into smoke consisting of an oxide of phosphorus, but if it is touched with a lighted match it takes fire and burns very rapidly, giving out much heat in its combustion. The product is the same in both cases; namely, oxide of phosphorus. Apparently the difference lies in the amount of heat given off, but very accurate experiments demonstrate that this, too, is *exactly the same*. In the one case the action is so slow that the heat is conducted away as fast as it is liberated, and so it escapes notice; in the other it is given off so rapidly as to be very

striking. A similar relation has been found to hold true in all cases of combustion. *The heat given off in oxidation is exactly the same whether the action is fast or slow, provided the same compound is formed.*

Spontaneous combustion. It has been found that the rate at which oxidation goes on is greatly increased by raising the temperature of the material undergoing oxidation. Consequently, if the conditions surrounding oxidation are such that the heat given

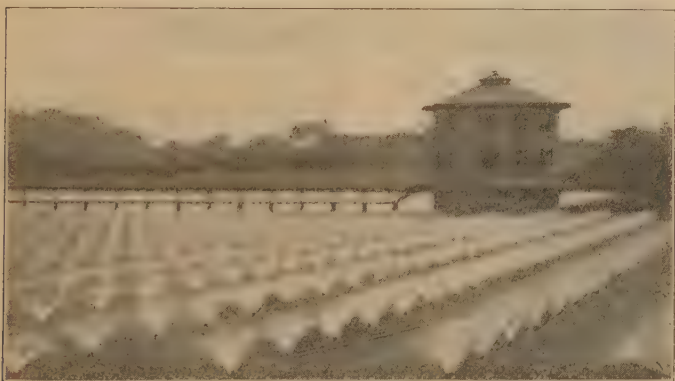


FIG. 14. Sewage-disposal plant at Columbus, Ohio, in which the sewage is sprayed into the air to secure its oxidation

off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature, until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature*. Materials taking fire in this way are said to undergo *spontaneous combustion*. It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation. Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine, dry coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm, dry place. Sometimes

the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or barn if the hay is not well dried before storing.

Importance of oxygen. Oxygen is one of the most important of the elements. It is essential to all forms of life except certain low forms of plant life. In the presence of certain minute



FIG. 15. An aviator fitted with an oxygen container and a device for breathing pure oxygen

microörganisms, which in some way assist in the process, the oxygen in the air acts upon the dead products of animal and vegetable life and converts them into harmless substances. In this way it acts as a purifying agent. For example, in sewage-disposal plants, sewage is forced into the atmosphere in fine sprays (Fig. 14) so that the oxygen can come in contact with the putrid matter in the sewage, thus purifying the sewage and preventing it from becoming a menace to health. Pure oxygen is used in the treatment of certain diseases in which the patient is unable to inhale sufficient air to supply

the necessary quantity of oxygen. Aviators are supplied with the pure gas for use at high altitudes (Fig. 15). The gas is also used as a source of intense heat as well as in the manufacture of certain compounds. Thus large quantities were used during the World War in the preparation of the poison gas known as *phosgene*, which is a compound of oxygen, chlorine, and carbon.

Solution of chemical problems. We have seen that every pure compound has a perfectly definite composition, no matter

what may be the source of the compound. The only way to determine the composition of any compound is by experiment, but having once determined the composition of any individual compound in the laboratory it is possible to solve certain problems in which the compound is involved. Thus, suppose we wish to know what weight of potassium chlorate is necessary for the preparation of 100 g. of oxygen. As already stated (p. 16), the composition of potassium chlorate as determined by experiment is as follows: potassium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. In other words, 100 g. of potassium chlorate contains 39.2 g. of oxygen. To prepare 1 g. of oxygen would require, therefore, $100 \div 39.2$, or 2.55 g., of potassium chlorate. To prepare 100 g. of oxygen then would require 2.55×100 , or 255 g., of potassium chlorate.

It must be kept in mind that the composition of a compound is always expressed in *percentage by weight*. If we wish to calculate what weight of potassium chlorate is necessary for the preparation of, say, 100 *liters* of oxygen, it is first necessary to calculate the weight of the 100 liters of the gas. By referring to the Appendix it will be found that 1 liter of oxygen weighs 1.429 g., hence 100 liters of oxygen weighs 100×1.429 , or 142.9 g. It is then easily possible by the method described above to calculate the weight of potassium chlorate necessary to prepare the 142.9 g. of oxygen.



EXERCISES

1. From your everyday experiences state how it is possible to change the volume of a gas.
2. The statement is made in the text that 1 liter of oxygen weighs 1.429 g. at a temperature of 0° and under a pressure of 1 atmosphere. Why is it necessary to say anything about the temperature and pressure?
3. Give the approximate weight of oxygen in your body.
4. (a) In Fig. 8 why does the water stay in the inverted cylinder? (b) Why does the oxygen displace it? (c) When a little oxygen has entered the cylinder why does not all the water run out?
5. Give the derivation of the following words: (a) pneumatic, (b) catalysis, (c) phlogiston. (See dictionary.)

6. Can you tell from the properties of a compound whether or not it contains oxygen?

7. Neither sulfur nor oxygen has any odor. How do you account for the odor noticeable when the sulfur burns in oxygen?

8. Suggest a simple way of proving that water is formed when a candle burns.

9. (a) How do you account for the fact that when a lamp is lighted a film of moisture is deposited on the chimney? (b) Is the film deposited on the inside or the outside of the chimney? (c) Why does the film soon disappear?

10. When ice water is poured into a goblet, moisture often collects on the outside of the goblet. What is the source of this moisture?

11. What simple facts or experiments disprove the phlogiston theory?

12. How would you collect a gas that is soluble in water?

13. Since oxygen is so active, why is the free element present in the atmosphere in such large quantities?

14. Why do certain substances form ashes on burning, while others do not?

15. Can you suggest a reason why some coals when burned leave more ashes than others?

16. Can combustion take place without the emission of light?

17. Is the evolution of light always produced by combustion?

18. Suggest a simple test for pure oxygen.

19. Distinguish between the terms (a) oxide, (b) oxidation, (c) combustion, (d) products of combustion.

20. How can you account for the explosion of fuel gas?

21. Machines used for threshing wheat have been known to explode with great violence when in operation. Suggest a cause for the explosion.

22. Why do substances burn more readily in pure oxygen than in air?

23. Why are oily rags more likely to start a fire than oil spilled on the floor?

24. For what purposes is oxygen used in automobile repair shops?

25. Calculate the weight of 50 liters of oxygen.

26. Calculate the volume of 50 g. of oxygen (unless otherwise noted it will be understood that all volumes will be measured at 0° and under a pressure of 1 atmosphere).

27. How large a bottle measured in cubic centimeters will 1 g. of oxygen fill?

28. State how many grams of oxygen are present in 100 g. of each of the following compounds: (a) mercuric oxide; (b) potassium chlorate; (c) water. (Calculate from percentages of these compounds given in the text.)

29. (a) 1 g. of potassium chlorate will yield on heating what weight of oxygen? (b) What volume in cubic centimeters will this weight of oxygen occupy?

30. An aviator wishes to take with him in his flight 100 liters of oxygen. What weight of potassium chlorate will be required for the preparation of this volume of oxygen? (Use the data obtained in problem 29 for the calculation.)

31. A student wishes to fill five bottles with oxygen, each bottle holding 500 cc. What weight of potassium chlorate will be required to prepare this volume of oxygen?

32. Suppose you heated 100 g. of potassium chlorate in a flask until all the oxygen is evolved. (a) What compound remains in the flask? (b) Calculate the weight of this compound.

33. A student prepared oxygen by heating a mixture of 10 g. of potassium chlorate and 2 g. of manganese dioxide. (a) What weight of oxygen was obtained? (b) What compounds remained in the flask? (c) Calculate the weight of each.

34. What is the approximate volume of 100 g. of water (see discussion of metric system in Appendix). Suppose you decompose this water by electrolysis. (a) What volume of oxygen would be obtained? (b) Compare the volume of the water with that of the oxygen obtained from it.

CHAPTER IV

HYDROGEN

Introduction. A great variety of materials undergo combustion, among them being coal, wood, oils, and various gases. One of these combustible gases, hydrogen, is of special interest because it is an elementary substance.

Properties of hydrogen. Hydrogen resembles oxygen in that it is a colorless, tasteless, odorless gas. *It is the lightest of all known substances*, 1 liter of the gas weighing only 0.08987 g. Soap bubbles blown with hydrogen rapidly rise in the air, as do also balloons filled with the gas. The solubility of hydrogen in water is very slight, being still less than that of oxygen. Pure hydrogen produces no injurious results when inhaled. Of course one could not live in an atmosphere of the gas, since oxygen is essential to respiration.

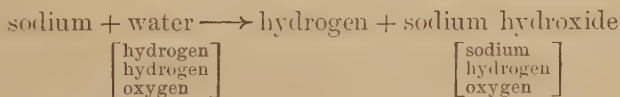
Occurrence. Free hydrogen occurs in enormous quantities in the gases surrounding the sun and certain other stars. In the combined state it is widely distributed, being a constituent of water as well as of all living organisms and of many of the products derived from them, such as wood, starch, and sugar. About 10 per cent of the human body is hydrogen, largely in the form of water. Combined with carbon it forms many compounds, which, mixed together, constitute petroleum and natural gas. Traces of free hydrogen also occur in the atmosphere.

Historical. Various combustible gases have been known from early ages, but they were long confused with each other. The gas hydrogen was first clearly recognized as a distinct substance by the English investigator Cavendish in 1766;

he obtained it in pure condition and showed it to be different from all other known gases. It was named hydrogen by Lavoisier, the word meaning "producer of water."

Preparation. Hydrogen can be prepared in a number of ways, the most important of which are the following:

1. **Preparation from water.** Since water contains hydrogen and is so abundant it is but natural that we should try to obtain the element from this source. It is possible to liberate the hydrogen in water in two general ways: (*a*) In the first place we may use the method of electrolysis already described (Fig. 9) and in this way obtain both hydrogen and oxygen, or (*b*) we may act on water with certain elements which will combine with the oxygen of the water and liberate the hydrogen. For this purpose some of the metals serve our purpose best. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a bit of the metal *sodium* is dropped on water, an action is seen to take place at once, sufficient heat being set free to melt the sodium, which runs about on the surface of the water. The change which takes place consists in the substitution of one half of the hydrogen of the water by the sodium, and may be represented as follows:



The sodium hydroxide formed is a white solid which remains dissolved in the excess of undecomposed water and may be obtained by evaporating the solution to dryness. The hydrogen is evolved as a gas and may be collected by suitable means.

Fig. 16 represents a simple form of apparatus used in preparing hydrogen by the action of sodium on water. Since the sodium is lighter than water, it is kept under the water by pushing a pellet

of the metal into one end of a short piece of lead or tin pipe, the other end of which has been hammered until closed. The pipe containing the sodium is then dropped into a trough of water. Hydrogen is at once evolved and is collected by bringing over it a bottle or cylinder filled with water, as shown in the figure.

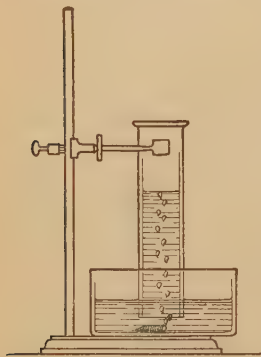
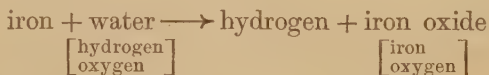


FIG. 16. The preparation of hydrogen by the action of sodium on water

Other metals, such as *magnesium* and *iron*, decompose water rapidly but only at higher temperatures. When steam is passed over hot iron, for example, the iron combines with the oxygen of the steam, setting free all the hydrogen. Experiments show that the change may be represented as follows:



The iron oxide formed is a reddish-black compound identical with that obtained by the combustion of iron in oxygen.

Preparation of hydrogen from iron and steam. The apparatus used in the preparation of hydrogen from iron and steam is shown in Fig. 17. A porcelain or iron tube *A*, about 50 cm. in length and 2 cm. or 3 cm. in diameter, is partly filled with fine iron wire or tacks and connected as shown in the figure. The tube is heated slowly at first, until the iron is red-hot. Steam is then conducted through the tube by boiling the water in the flask *B*. The hot iron combines with the oxygen in the steam, setting free the hydrogen, which is collected over water in *C*.

2. Preparation from acids (usual laboratory method). The *acids* constitute a very important class of compounds, and we shall be much concerned with them later in our study. For the present it is only necessary to know that they all contain hydrogen and that certain metals when brought in contact

with them dissolve, and in the change which takes place the hydrogen of the acid is liberated. This constitutes a very convenient method for preparing hydrogen in the laboratory.

It has been found most convenient and economical in preparing hydrogen by this method to use either *zinc* or *iron* as the metal and either *hydrochloric acid* or *sulfuric acid* as the acid. Hydrochloric acid is an aqueous solution of a gaseous

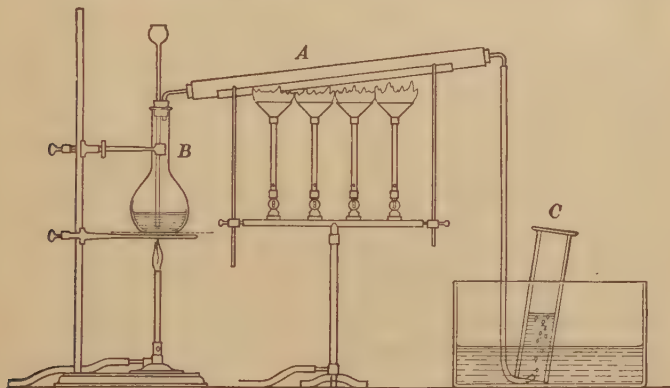
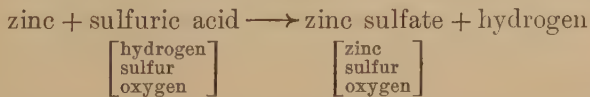


FIG. 17. The preparation of hydrogen by passing steam over hot iron

compound known as hydrogen chloride (which consists of 2.77 per cent hydrogen and 97.23 per cent chlorine), while sulfuric acid is an aqueous solution of an oily liquid known as hydrogen sulfate (which consists of 2.05 per cent hydrogen, 32.70 per cent sulfur, and 65.25 per cent oxygen).

The changes taking place in the preparation of hydrogen from zinc and sulfuric acid may be represented as follows:



In other words, the zinc takes the place of the hydrogen in sulfuric acid. The resulting compound contains zinc, sulfur,

and oxygen and is known as *zinc sulfate*. This remains dissolved in the water in the acid. It may be obtained in the form of a white solid by evaporating the liquid left after the metal has passed into solution.

Directions for preparing hydrogen from acids. The preparation of hydrogen from acids is carried out in the laboratory as follows:

The metal is placed in a flask or wide-mouthed bottle *A* (Fig. 18), and the acid is added slowly through the funnel tube *B*. The metal dissolves in the acid, while the hydrogen which is liberated escapes through the exit tube *C* and is collected over water.

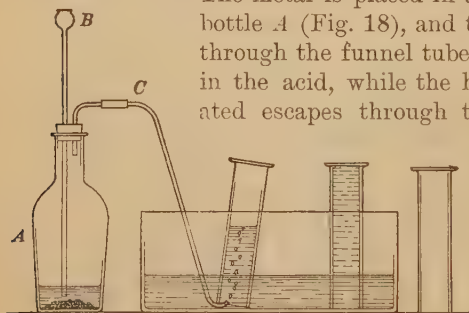


FIG. 18. The preparation of hydrogen by the action of metals on acids

Commercial preparation. Both of the general methods of preparation described above have been used in preparing hydrogen on a large scale,

but these have been largely displaced by cheaper methods recently developed. The reactions involved are too complicated to describe at the present time, but will be referred to in a later chapter.

Chemical conduct. At ordinary temperatures hydrogen is not an active element. Under suitable conditions, however, it combines with a number of the elements, forming many important compounds. Thus, hydrogen and chlorine, when mixed together, will combine with explosive violence if heated or if exposed to the sunlight. The product formed in either case is called *hydrogen chloride*. Under suitable conditions hydrogen combines with nitrogen to form *ammonia* and with sulfur to form the foul-smelling gas *hydrogen sulfide*. At ordinary temperatures hydrogen and oxygen may be mixed without action. If the mixture is heated to about 800° , or if a flame is brought

in contact with it, a violent explosion takes place. Nevertheless, under proper conditions hydrogen may be made to burn quietly in either oxygen or air. The flame produced by the combination is almost colorless and is very hot. The combustion of the hydrogen is due to its union with oxygen, and the product of the combustion is an oxide of hydrogen. That this compound is water may be easily shown by experiment.

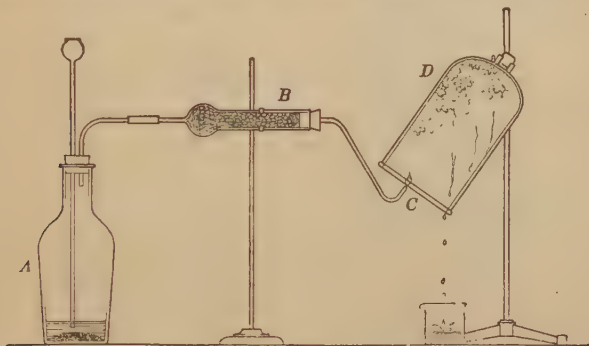


FIG. 19. Burning hydrogen in air and collecting the product of its combustion (water)

Directions for burning hydrogen. The combustion of hydrogen in air may be carried out safely as follows: The hydrogen is generated in the bottle *A* (Fig. 19), is dried by conducting it through the tube *B* filled with some substance (usually calcium chloride) which has a great attraction for moisture, and escapes through the tube *C*, the end of which is drawn out to a jet. *When all the air has been expelled from the apparatus the hydrogen may be ignited.* It then burns quietly, since only the small amount of it which escapes from the jet can come in contact with the oxygen of the air at any one time. By holding a cold, dry bell jar or bottle over the flame in the manner shown in the figure, the steam formed by the combustion of the hydrogen is condensed, water collecting in drops on the sides of the jar.

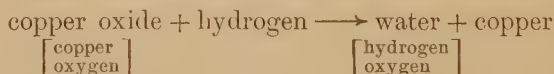
Hydrogen not a supporter of combustion. While hydrogen is readily combustible, it is not a supporter of combustion; in

other words, substances will not burn in it. This may be shown by bringing a lighted candle supported by a stiff wire into a bottle or cylinder of the pure gas, as shown in Fig. 20. The hydrogen is ignited by the flame of the candle and burns at the mouth of the cylinder, where it comes in contact with the oxygen in the air. When the candle is thrust up into the gas its flame is extinguished. If slowly withdrawn, the candle is relighted as it passes through the layer of burning hydrogen.



FIG. 20. Flame of a candle extinguished by hydrogen

Reduction. On account of its tendency to combine with oxygen, hydrogen has the power of abstracting it from many of its compounds. Thus, if a stream of hydrogen generated in *A* (Fig. 21) and dried by passing through the tube *B* (filled with calcium chloride) is conducted through the tube *C*, which contains some copper oxide heated to a moderate temperature, the hydrogen takes away the oxygen from the copper oxide. The change may be represented as follows:



The water formed collects in the cold portions of the tube *C*, near its end, and drops into the glass. In this experiment the copper oxide is said to undergo *reduction*. *Reduction may therefore be defined as the process*

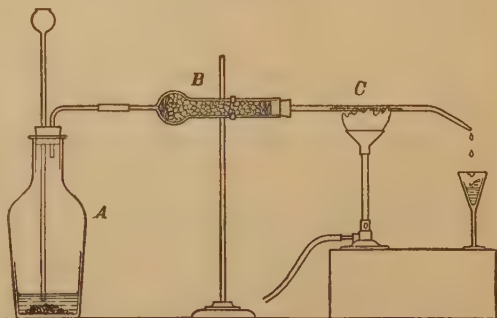


FIG. 21. The reduction of hot copper oxide by a stream of hydrogen

of *withdrawing oxygen from a compound*. As we shall see, the term *reduction* is also used with a somewhat different meaning.

Relation of reduction to oxidation. At the same time that the copper oxide is reduced, it is clear that the hydrogen is oxidized, for it combines with the oxygen given up by the copper oxide. The two processes are therefore very closely related, and it usually happens that when one substance is oxidized another substance taking part in the reaction is reduced. The one which gives up its oxygen is called an *oxidizing agent*, while the other, which unites with the oxygen of the oxidizing agent, is called a *reducing agent*.

The oxyhydrogen blowpipe; the blast lamp. The *oxyhydrogen blowpipe* is a device for burning pure hydrogen in pure oxygen. It was devised by the American chemist Robert Hare (Fig. 22) in 1801 and was formerly used as a source of intense heat. A similarly constructed apparatus, known as the *blast lamp*, is now used in all laboratories (Fig. 23). It consists of two tubes, one inside the other. Coal gas or natural gas (both of which are gaseous compounds of hydrogen) is forced through the inner tube (Fig. 23) and lighted. Air is then forced through the outer tube in quantities sufficient to burn the gas.

Uses of hydrogen. Hydrogen is used for inflating balloons and dirigible airships such as the Zeppelins, so largely used in the World War (Fig. 7). Its chief peace-time use is in the refining of certain oils, such as cottonseed oil, whereby these oils

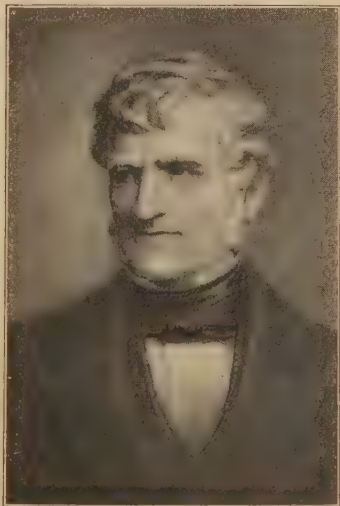


FIG. 22. Robert Hare (1781-1858)

An early American chemist; the inventor of a number of ingenious laboratory appliances, including the oxyhydrogen blowpipe

are not only purified but are transformed into solid fats which may be used in cooking to replace lard (see hydrogenation of oils). Hydrogen is also coming into use in the preparation of ammonia, as will be explained later.

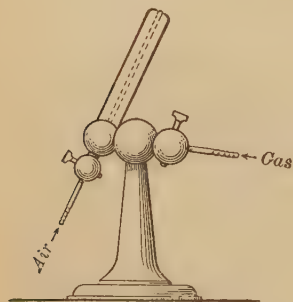


FIG. 23. The ordinary laboratory blast lamp

Further statements concerning the solution of chemical problems. Many compounds can be made by the direct union of the elements present in the compound. Thus, hydrogen and oxygen unite directly to form water. Knowing the composition of the compound, one can tell in what proportion the elements will combine to form the compound.

Thus the composition of water, as determined by experiment, is hydrogen 11.19 per cent and oxygen 88.81 per cent; in other words, 11.19 g. of hydrogen will combine with 88.81 g. of oxygen to form 100 g. of water. If the two gases are brought together in other proportions than these and ignited, combination will take place, but a definite amount of the gas in excess will be left uncombined. For example, if 11.19 g. of hydrogen were mixed with, say, 125 g. of oxygen, only 88.81 g. of the oxygen would enter into combination with the hydrogen, leaving $125 - 88.81$, or 36.19 g., of oxygen uncombined.

EXERCISES

1. (a) What is the approximate weight of the hydrogen present in your body? (b) In what form is most of it found?
2. What per cent of water, by weight, is hydrogen?
3. (a) What element other than hydrogen did Lavoisier name? (b) What was Lavoisier's greatest contribution to chemistry?
4. Should you expect hydrogen and oxygen to occur together in a free state in nature?

5. In preparing hydrogen as illustrated in Fig. 17 do you see any reason why the tube *A* should be inclined as represented in the figure?

6. (a) In preparing hydrogen according to Fig. 18 what is the composition of the gas that at first escapes through the tube *C*? (b) Is such a gas explosive, and, if so, under what conditions?

7. Contrast the properties of hydrogen and oxygen.

8. What factors determine the choice of the method used for preparing a substance commercially: that is, on a large scale?

9. In Fig. 19 why is it necessary to dry the hydrogen by means of calcium chloride in the tube *B*?

10. From Fig. 21 suggest a way for determining by experiment the weight of water formed in the reaction.

11. Why does a mixture of hydrogen and oxygen explode more violently than a mixture of hydrogen and air?

12. Weight for weight, which will yield the greatest volume of hydrogen: hydrogen chloride, hydrogen sulfate, or water?

13. Contrast the terms (a) *oxidation* and *reduction*; (b) *oxidizing agent* and *reducing agent*.

14. Why does the oxyhydrogen blowpipe give a hotter flame than the blast lamp?

15. (a) Would the relative proportions of hydrogen and oxygen used in an oxyhydrogen blowpipe make any difference in the intensity of heat obtained? (b) If so, what proportions would give the best results?

16. What is a serious objection to the use of hydrogen for inflating balloons used for war purposes?

17. How much heavier is oxygen than hydrogen?

18. Calculate the weight of 50 liters of hydrogen.

19. Calculate the volume of 50 g. of hydrogen.

20. How large a bottle, measured in cubic centimeters, will 1 g. of hydrogen fill? (Compare with exercise 27 of the preceding chapter.)

21. (a) What weight of hydrogen is present in 100 g. of hydrogen chloride? (b) If liberated, what volume would this occupy?

22. One gram of hydrogen chloride will yield (a) what weight of hydrogen? (b) what volume of hydrogen?

23. One gram of hydrogen sulfate will yield (a) what weight of hydrogen? (b) what volume of hydrogen?

24. A student wishes to fill five bottles with hydrogen, each holding 1 liter. What weight of hydrogen sulfate will be required for its preparation?

25. The dirigible *R-34* (see Fig. 7) has a capacity of 2,000,000 cubic feet. One cubic foot equals 28.32 liters. Calculate the weight in kilograms of hydrogen sulfate required to prepare sufficient hydrogen to fill the dirigible.

26. One gram of hydrogen is mixed with 20 g. of oxygen and the mixture is exploded. Calculate the weight of water formed.

27. Hydrogen and chlorine unite to form the gas known as hydrogen chloride. (a) 100 g. of hydrogen will combine with how many grams of chlorine (p. 33)? (b) How many grams of hydrogen chloride will be formed?

28. Suppose that 10 l. of hydrogen were passed over copper oxide (Fig. 21) and that all the hydrogen combined with oxygen in the copper oxide to form water. What weight of water would be formed?

29. Suppose that 10 g. of water were decomposed by electrolysis (Fig. 9). (a) What weight of hydrogen and oxygen respectively would be formed (p. 18)? (b) What volumes would the hydrogen and oxygen occupy?

CHAPTER V

HOW GASES ACT; HOW THEY ARE MADE UP

Introduction. It will be remembered that in describing the properties of oxygen and hydrogen the weight of one liter of each gas was given. A moment's reflection will make it clear that these weights must refer to some set of arbitrary conditions, for it is a familiar fact that the volume of a given quantity of a gas varies both with changes in pressure and with changes in temperature. Consequently the weight of a liter of a gas must also be variable.

Variation of volume with pressure: law of Boyle. That the volume occupied by a given weight of a gas can be altered by changing the pressure is familiar to everyone who has pumped air into a bicycle or automobile tire. As early as 1660 Robert Boyle, an English

investigator (Fig. 24), reached the following conclusion, known as Boyle's law: *The volume occupied by a given weight of a gas is inversely proportional to the pressure, provided the temperature remains constant.* Thus, if a given weight of a gas occupies a volume of 1000 cc. when subjected to a certain pressure, it will occupy a volume of 500 cc. if the pressure is doubled, or



FIG. 24. Robert Boyle (1627-1691)

One of the most accurate of the early experimenters in chemistry and physics

of 2000 cc. if the pressure is diminished to one half. This means that for a given weight of a gas the product of the pressure into the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by P and V , and under a different set by P_1 and V_1 , Boyle's law may be stated thus:

$$PV = P_1V_1$$

It is a remarkable fact that all gases act in this same way.

Standard pressure. For practical purposes, therefore, we must choose some standard pressure under which we will agree to measure all gas volumes. This is most conveniently chosen as the average pressure of the atmosphere at the sea level. This is equal to 1033 g. per square centimeter. In place of expressing the pressure in this way it is much more convenient to express it in terms of the height of the column of mercury which the pressure of the atmosphere will sustain. Expressed in this way the standard pressure is equal to that exerted by a column of mercury 760 mm. in height, this being the average height of the barometer at the sea level.

Illustration of the law of Boyle. The following example will not only make the meaning of the law clear but will also show how the law enables us to calculate the changes in the volume of a gas due to changes in pressure:

A gas measured under a pressure of 720 mm. had a volume of 620 cc. What volume will this gas occupy under standard pressure, 760 mm., the temperature remaining constant?

According to Boyle's law, $PV = P_1V_1$. Substituting the values given in the problem, we have $760 \times V = 720 \times 620$, or $V = 587.4$ cc.

Variation of volume with temperature. If the pressure is held constant, all gases expand when the temperature is raised and contract, when it is lowered, and it is a remarkable fact that the volumes of all gases change to the same extent for

a given variation in the temperature. Let us suppose that the volume of a gas has been measured at 0° on the centigrade scale. Experiment has shown that for each degree the temperature is raised above 0° , the volume of the gas increases by $\frac{1}{273}$ of the volume it occupied at 0° . Similarly, for each degree the temperature is lowered below 0° , the volume diminishes by $\frac{1}{273}$ of the volume it occupied at 0° . To take a simple illustration: If the volume of a gas at 0° is 273 cc., then at 1° it will be 274 cc., while at -1° it will be 272 cc. At 5° it will be 278 cc., while at -5° it will be 268 cc. It is evident, then, that at this rate of change the volume at -273° will be zero. Of course this cannot really happen, and experiment shows that before this temperature is reached, all gases have changed into liquids or solids. Helium, the most difficult gas to liquefy, passes into a liquid at -268.7° .

The absolute scale. For many purposes it has been found convenient to use a new scale of temperature known as the *absolute scale*, on which the divisions are of the same size as those on the centigrade scale, but the zero point is the same as -273° on the centigrade scale; that is, the temperature at which the volume of any gas would apparently become zero (see preceding paragraph). The 0° on the centigrade scale would then be 273° on the absolute scale. On such a scale all temperatures are above the zero point. To convert readings on the centigrade scale to the corresponding

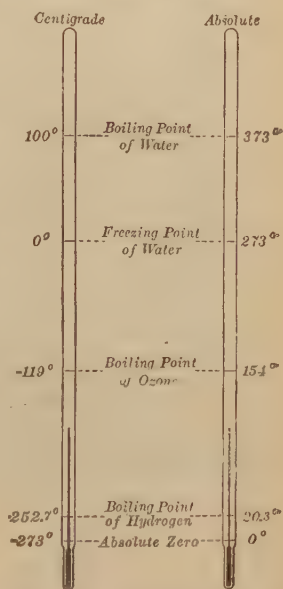


FIG. 25. Comparison of the centigrade with the absolute scale of temperature

ones on the absolute it is only necessary to add 273. Thus, $20^{\circ}\text{C.} = 20 + 273^{\circ}$, or 293°A. , while $-20^{\circ} = -20 + 273$, or 253°A. Fig. 25 gives a comparison of the centigrade and absolute scales at a number of temperatures.

The law of Gay-Lussac (or of Charles). A general statement can now be made in regard to the effect of temperature on the

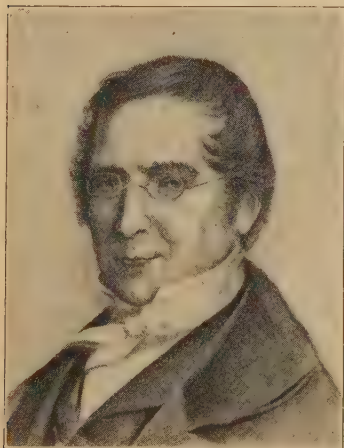


FIG. 26. Joseph Louis Gay-Lussac
(1778-1850)

A distinguished French chemist who contributed much to our knowledge of gases and their combining ratios

volume of a gas: *The volumes occupied by a given weight of a gas at different temperatures are proportional to the absolute temperatures, provided the pressure remains constant.* If V and V_1 are the volumes at the temperatures T and T_1 , then $V:V_1 = T:T_1$,

$$\text{or} \quad V = \frac{V_1 T}{T_1}$$

The above generalization is called the law of Gay-Lussac (Fig. 26) or of Charles, since it was formulated independently by these Frenchmen in 1801.

Illustration of the law of Gay-Lussac. The following example will make the meaning of the law clear. The volume of a certain gas measured at a temperature of 70° is 650 cc. What will be its volume at 10° , the pressure remaining unchanged?

First reduce the centigrade readings to absolute:

$$70^{\circ}\text{C.} = 70 + 273 = 343^{\circ}\text{A.}; \quad 10^{\circ}\text{C.} = 10 + 273 = 283^{\circ}\text{A.}$$

Then substitute the appropriate values in the above equation:

$$V = \frac{650 \times 283}{343}, \text{ or } V = 536.3 \text{ cc.}$$

Variations in volume due to changes both in pressure and temperature. In case both pressure and temperature change, then the correction may be made for each in succession, as illustrated in the following example:

A certain weight of gas measured 500 cc. at a temperature of 100° when subjected to a pressure of 760 mm. Calculate the volume which this gas will occupy at a temperature of 50° and a pressure of 740 mm.

First make the correction for pressure:

$$PV = P_1V_1$$

$$740 \times V = 760 \times 500, \text{ or } V = 513.5 \text{ cc.}$$

Next make the correction for temperature:

$$V = \frac{V_1T}{T_1}, \text{ or } V = \frac{513.5 \times 323}{373}, \text{ or } V = 444.6 \text{ cc.}$$

Standard conditions. Since the volume of a gas varies with both temperature and pressure, it is essential that we select both a *standard temperature* and a *standard pressure* to which we shall agree to refer all gas volumes. We have already noted that the *standard pressure adopted is that exerted by a column of mercury 760 mm. in height. As a standard temperature, the temperature of melting ice is chosen.* This is 0° centigrade or 273° absolute. Whenever the volume of a gas is given it is always assumed, unless otherwise specified, that the volume given is that occupied by the gas under standard conditions.

Vapor pressure of water. As a rule gases are measured in the laboratory by collecting them over water in a graduated tube, as represented in Fig. 27. Before the reading is taken the tube *A* is first raised or lowered until the level of the water is the same within and without the tube; the inclosed gas is then under atmospheric pressure. But to some extent water has evaporated into the tube, and a part of the volume inclosed is *due to water vapor* and not to the gas. If the water vapor could be removed, the gas would occupy a

smaller volume. The downward pressure upon the water in the tube *A* is partly due to the pressure exerted by the gas and partly to the pressure exerted by the water vapor. If

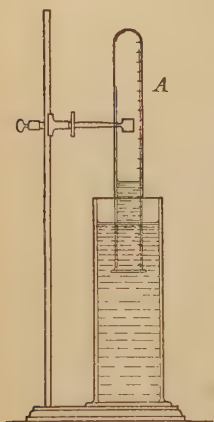


FIG. 27. Measuring a volume of gas collected over water

we could find out how much pressure the water vapor exerts upon the surface of the water within the tube and subtract this from the atmospheric pressure, we should have the pressure which the gas itself exerts at the volume which it occupies. The pressure due to the water vapor is called the *vapor pressure of water*. It increases steadily as the temperature rises, and the table in the Appendix gives its value over the usual range of temperatures that occurs in the laboratory.

Solution of problems involving calculation of volumes of gases collected over water. By referring to Fig. 27 it is evident that the atmosphere pressing down upon the surface of the water in the cylinder tends to force the water up in the tube *A* and so compresses the gas in the tube. The aqueous vapor mixed with the gas within the tube tends to push the water down and thus acts in opposition to the atmospheric pressure. It is evident, therefore, that to obtain the value of the effective pressure to which the gas in the tube is subjected, we must subtract the value of the vapor pressure of water from the value of the pressure indicated by the barometer. The following example will make this clear:

A gas measured over water has a volume of 300 cc. when the barometer reads 740 mm. and the thermometer 20°. Calculate the volume which the gas will occupy if the pressure is increased to 760 mm., the temperature remaining constant. The effective pressure on the gas equals 740 mm. less the vapor pressure of water at 20°, which is 17.51 mm. (Appendix), or $740 - 17.51 = 722.49$ mm. Substituting these values in the equation expressing Boyle's law, we have

$$V \times 760 = 722.49 \times 300, \text{ or } V = 285 \text{ cc.}$$



FIG. 28. Amedeo Avogadro (1776-1856)

A celebrated Italian scientist who first advanced the fundamental principle of modern chemistry known as Avogadro's Principle. He was professor in the University of Turin, Italy. The engraving is from a photograph of a statue erected at Turin to his memory

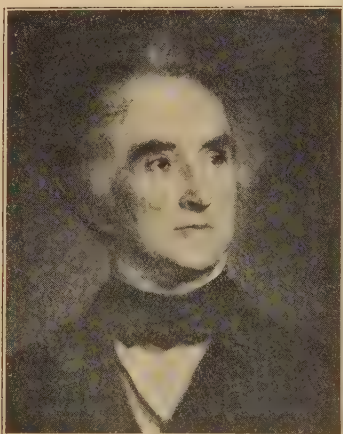


FIG. 29. Justus Liebig
(1803-1873)

A great German chemist and teacher. A pioneer chemist, especially in the application of chemistry to agriculture



FIG. 30. Michael Faraday
(1791-1867)

A distinguished English chemist and physicist. Noted especially for his study of electrolysis. He discovered a number of compounds, including benzene, from which most aniline dyes are prepared. He was the first to study the methods of liquefying gases and was very skillful in performing experiments

Nature of gases ; Avogadro's principle. It is a surprising fact that all gases are equally affected by changes in temperature and pressure. This property of gases suggests that there must be some marked similarity in the make-up of all gases. The most likely guess about this that anyone could think of was advanced many years ago and was known as the *kinetic theory*. The main points of this theory are as follows: (1) all gases are made up of minute particles called *molecules*; (2) all the molecules of any definite gas are identical in every way, but the molecules of different gases differ at least in weight and composition; (3) the molecules are in very rapid motion, constantly hitting each other as well as the sides of any containing vessel; (4) when a gas is heated, the motion of the molecules is increased. In accordance with this idea of a gas, the molecules do not completely fill all the space in which they are confined, just as the people in a room do not fill all the space in the room. If the gas is compressed, the molecules are not changed in any way, but are simply crowded more closely together. One may get a rough idea of the make-up of a gas in which the molecules are enormously magnified by noting the conditions that exist in a swarm of bees. The swarm is made up of individual bees all alike and all in rapid motion.

The above view of matter, although originally advanced as a plausible guess, is now known to be true. Indeed, we can count the molecules and even approximate their weight. Moreover, we know that *equal volumes of all gases under the same conditions of temperature and pressure inclose the same number of molecules*. This view, originally advanced by the Italian scientist Avogadro (Fig. 28), is now known to be a statement of fact and is termed *Avogadro's principle*. It is a very important fact, and we shall refer to it in later chapters. We shall find later that solids and liquids also are made up of molecules, but in these the molecules are closer together and not in such rapid motion. *Avogadro's principle, however, applies only to gases.*

EXERCISES

NOTE. All temperatures are expressed in the centigrade system unless otherwise stated. In solving problems the student will take into account the vapor pressure of water only when the statement is made that the gas is collected over water.

1. Give two illustrations of Boyle's law from everyday experience.
2. Why is the bottom of a balloon left open and not tightly closed?
3. Why does a balloon tend to fall toward evening and rise at midday?
4. Why does the carburetor on a motor car have to be adjusted with changes in the atmospheric conditions in order to secure the greatest efficiency?
5. How could you prevent the expansion of a gas when heated?
6. Why is it not advisable to inflate automobile tires to as high pressures in summer as in winter?
7. How can you account for the explosion of a steam boiler?
8. What evidence can you give tending to show that the amount of water vapor taken up by a gas increases with the temperature?
9. What would be the effect of relieving a gas from any pressure whatever?
10. Show that the kinetic conception of gases is in accord with the facts stated in the law of Boyle and the law of Gay-Lussac.
11. A gas has a volume of 1 liter under a pressure of 730 mm. What will be its volume if the pressure is increased to standard (760 mm.), the temperature remaining constant?
12. In exercise 11 suppose that the gas had a volume of 1 liter measured over water at 20° . Calculate the volume of the dry gas under standard pressure, the temperature remaining constant. Compare your answer with that obtained in exercise 11.
13. A gas under standard pressure measured 500 cc. Calculate the pressure necessary to diminish the volume to 425 cc.
14. A gas measured 200 cc. in a laboratory in which the temperature was 20° . During the night the temperature fell to 15° , but the barometric pressure remained constant. What volume did the gas then occupy?
15. Fifty liters of oxygen at a temperature of 20° was heated until the temperature was 50° , the pressure remaining constant. Calculate its volume at this increased temperature.

16. A gas measured 200 cc. in a laboratory in which the thermometer registered 20° and the barometer 740 mm. Calculate its volume under standard conditions.

17. A student wishes to fill five bottles, each holding 1000 cc., with oxygen in a laboratory in which the temperature is 20° and the barometric reading is 750 mm. The gas must be collected over water. (a) What volume will this gas occupy under standard conditions? (b) What will this volume of oxygen weigh? (c) What weight of potassium chlorate will be necessary to prepare this weight of oxygen?

18. An automobile tire having a capacity of 1200 cu. in. is inflated to a pressure of 70 lb. per square inch. The temperature of the air at the time of inflation is 15° , but on rapid driving the temperature is increased to 40° . What is the pressure now exerted by the air in the tube, assuming that the volume of the tire remains constant? (Suggestion: First calculate the volume which 1200 cu. in. of air measured at 15° and a pressure of 70 lb. per square inch would occupy if the temperature were increased to 40° , the pressure remaining constant at 70 lb.; then calculate the pressure necessary in pounds per square inch in order to decrease this volume back to 1200 cu. in., the temperature remaining at 40° . The calculation may be simplified in the following way: Recall that the volume of a gas varies with the pressure, also with the absolute temperature. In the case of the tire, however, the volume is constant; hence the pressure will vary directly with the absolute temperature; that is,

$$P : P_1 = T : T_1$$

Substitute in the above equation, and solve for P .)

CHAPTER VI

MATTER AND ENERGY

Conservation of matter. We have seen that matter may be defined as anything that has weight or occupies space (p. 6) and that the chemist is interested in the various changes which matter undergoes (p. 1). A great many careful experiments have proved that while the form and the properties of matter change as a result of chemical action, the *amount* of matter (that is, its *mass*) remains constant. To put it in another way: no one has yet discovered any way of creating or destroying matter. This very important truth, first clearly recognized by Lavoisier, is known as the *law of conservation of matter*. This law may be stated thus: *In all the changes through which a given quantity of matter may pass, its mass remains unchanged.*

Mass and density. While the term *mass* as applied to matter means the *quantity of matter*, the term *density* means the mass *per unit volume*. In the metric system the unit of mass is the gram and the unit of volume is the cubic centimeter. In these units *the density of a substance is the number of grams in 1 cc. of the substance*. Since 1 cc. of water weighs very nearly 1 g., the number stating the density of a substance also gives, for all practical purposes, its weight as compared with an equal volume of water.

States of matter. It is well known that water may occur in three very different conditions, depending upon the temperature; namely, solid, liquid, and gaseous. These are called the *three states* of matter. This is not a peculiarity of water, for all substances exist in all three states, save only when the

temperature required for the melting of the solid or the vaporization of the liquid is so high that decomposition takes place before the change is effected. Thus we have seen that mercuric oxide decomposes before it melts. Potassium chlorate can be melted without difficulty, but it decomposes before it boils.

Freezing and melting points. A solid normally passes into a liquid at a perfectly definite temperature, called its *melting point*. A given weight of any solid, in melting, absorbs a definite quantity of heat, the exact amount absorbed depending upon the solid. This is known as the *heat of fusion*. On the other hand, the liquid formed tends to pass back into the solid state at this same temperature, called the *freezing point*, and in so doing the heat of fusion is given out again. In this case it is called the *heat of solidification*. For example, water freezes and ice melts at the same temperature; namely, 0° . Moreover, 1 g. of ice at 0° , in melting, absorbs a definite quantity of heat, while 1 g. of water at 0° , in freezing, gives out this same quantity of heat.

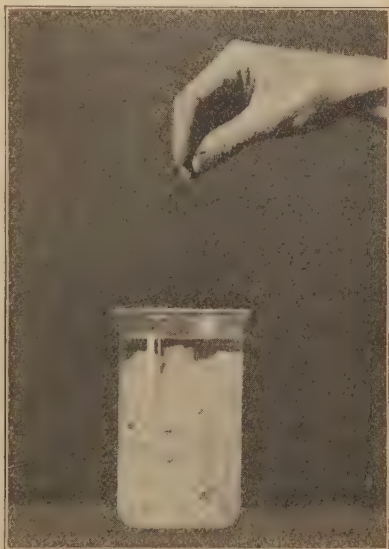


FIG. 31. A supercooled liquid quickly solidifies when a crystal of the solid is added

Sometimes it is possible to cool the liquid below the freezing point, and it is then said to be *undercooled*. If a fragment of the solid is dropped in the undercooled liquid, solidification will at once begin (Fig. 31), and the temperature will rise to the true freezing

point and remain there as solidification continues. The freezing point is therefore best defined as *the temperature at which the liquid and the solid can be mixed without change in temperature.*

Vaporization. There is no definite temperature at which a liquid passes into a vapor, or gas. *Water exposed to the air vaporizes at all temperatures*, and even ice and snow evaporate during weather in which no melting occurs. The higher the temperature, the more rapid the evaporation.

Boiling point. The escape of vapor from an open vessel containing a liquid is hindered by the air which presses upon the surface of the liquid. The vapor escapes by making its way slowly through the air, but when the vapor pressure just exceeds the pressure exerted by the air, there is nothing to prevent the vapor from making its escape as fast as it forms, pushing the air before it. When this is the case any additional heat applied to the liquid will not raise its temperature, but will merely increase its rate of evaporation.

This temperature is called the *boiling point* of the liquid, and the boiling point may be defined as *the temperature at which the vapor pressure of the liquid just exceeds the opposing pressure of the atmosphere.* It will be noticed that the boiling point of a liquid is not fixed, but depends upon the atmospheric pressure.

Liquefaction of gases. At ordinary pressures water above 100° is a gas. If it is either cooled or compressed, or both, it assumes the liquid state, and if cooled still further it assumes the solid state. This suggests that perhaps substances that are gases at ordinary temperature may be liquefied if cooled and compressed sufficiently. It is easy to show that this is true, at least in the case of some gases. For example, the gas known as sulfur dioxide assumes the liquid state when cooled to -8° at ordinary pressure, or if compressed sufficiently it liquefies at ordinary temperatures. For a long time some of the gases, such as hydrogen and oxygen, resisted all efforts to liquefy them and were known as *permanent gases*. At present, however, all

known gases have been liquefied and solidified. Liquid oxygen, for example, is a colorless liquid boiling at -183° , while liquid hydrogen is the lightest liquid known and boils at -252.7° .

At present machines are used for liquefying gases. These consist of an engine for compressing the gas and a *liquefier*, in which the gas is finally brought to the liquid state. The liquefier consists of a system of tubes and a valve so arranged that

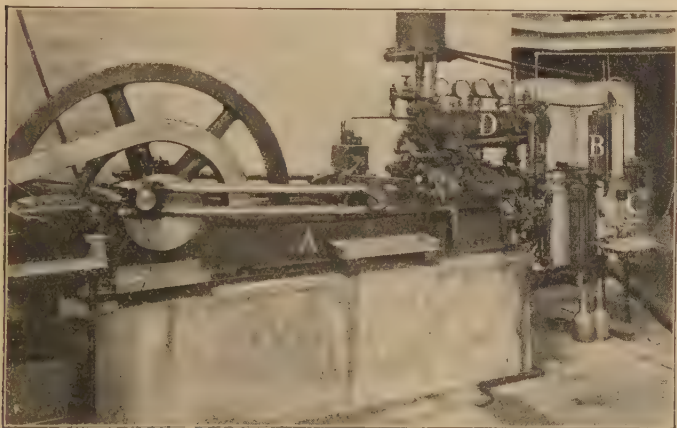


FIG. 32. A common type of apparatus used for liquefying air

when a portion of the compressed gas is allowed to escape through the valve the heat absorbed in the expansion of the escaping gas is taken from the remainder of the compressed gas. This process is continued until the gas is cooled sufficiently to become a liquid under the pressure used.

Fig. 32 shows a common form of apparatus used for liquefying air. The engine *A* compresses the air, the pressure being indicated by the gauges above *D*. A great deal of heat is generated in compressing the gas, and this is absorbed by cold water run through pipes in *D*. The compressed air then passes to the liquefier *B*, where it is liquefied. The liquid air flows from the liquefier into the Dewar flask *C*.

Dewar flasks; thermos bottles. Liquid air may be kept for some hours in a special form of flask devised by the Scottish scientist Dewar, known as a *Dewar flask*.



FIG. 33. A Dewar flask for holding liquid air

This consists of two concentric vessels (Fig. 33) of any convenient shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent heat conduction. The surface of the outer flask is often silvered in order to reflect the external heat and thus prevent its absorption. The so-called *thermos bottles* (Fig. 34) are constructed on the same plan and are very effective for keeping liquids either hot or cold for several hours.

Amorphous and crystalline matter. Sometimes the particles of which a piece of solid matter is composed have no definite form and even under the microscope show no sharp edges or flat surfaces. Such solids are said to be *amorphous*.

More often a careful examination of a solid will show that it is made up of a great many particles, each of which has sharp edges and flat surfaces. Such solids are said to be *crystalline*, and each individual piece is called a *crystal*. While crystals have a great variety of forms (Fig. 35), yet for any given substance the crystalline form is perfectly definite. Crystals range in sizes from microscopic to very large, a single quartz crystal found in California weighing over a ton.



FIG. 34. A thermos bottle

Energy. We sometimes say that a certain boy possesses a great deal of energy, meaning thereby that he has a great capacity for work. We recognize this same capacity for work

in inanimate things. Thus, steam highly compressed in a boiler moves the railway train. The electricity present in power lines moves the street car. While it is difficult to frame a satisfactory simple definition of energy, for our purposes we may define it as follows: *Energy is capacity for work, or the ability to do work.*

Transformation of energy. There are a great many forms of energy, such as the energy of heat, of electricity, of motion, and of light, for all these can perform work. Now it is entirely possible to convert each of these forms into the other forms ;



FIG. 35. Some typical examples of crystals

thus, it is the heat generated under the steam boiler that produces the motion of the machinery. The energy of the falling water at Niagara Falls produces electric energy, and this in turn is sent through the wires to factories, and there utilized for many purposes, such as producing light, heat, and motion.

Fig. 36 (p. 56) illustrates a few familiar transformations of energy. The heat of the flame *A* is converted into mechanical energy in the heat engine *B*. The motion of the engine is communicated to the small dynamo *C*, where it is converted into magnetic and electrical energy. The electrical energy is changed into heat and light in the incandescent lamp *D* and into chemical energy (p. 57) by the decomposition of water in *E*.

Conservation of energy. While it is thus possible to convert one form of energy into another, all the experiments performed show that in these transformations no energy is created or destroyed, but that a definite quantity of energy of one kind

always gives a definite and equivalent quantity of energy of another kind. This truth is known as the *law of the conservation of energy* and may be stated as follows: *Energy may be changed from one form to another, but it can be neither created nor destroyed.*

Measurement of energy. Since changes in energy are so constantly taking place all about us, it is a matter of great practical importance to devise units for the measurement of energy and methods for making the measurement. In general,

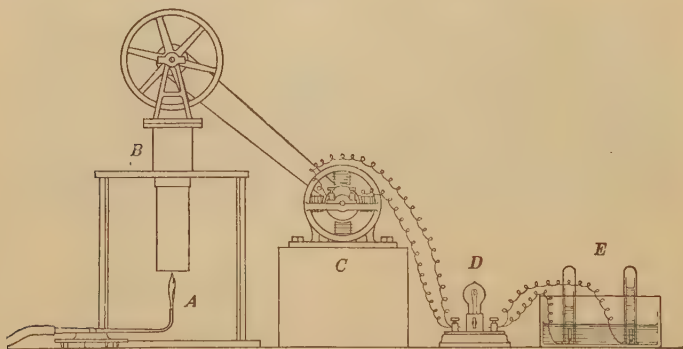


FIG. 36. Diagram illustrating some transformations of energy

each kind of energy must have its own units of measurement, just as with matter we have centimeters for lengths, liters for volumes, and grams for weights. In some of its forms energy is very difficult to measure directly. Indeed, neither units nor methods for the direct measurement of some forms of energy have as yet been devised. In such cases it is necessary to transform the energy into a form more convenient for measurement. In most cases it is changed into heat or electrical energy for this purpose, since these are easy to measure.

Measurement of heat. A quantity of heat energy is measured by observing to what extent it will change the temperature of a given mass of some standard substance. Water has

been chosen as the standard, and the unit of heat is called the *calorie* (designated by the abbreviation *cal.*). It is defined as *the quantity of heat required to change the temperature of one gram of water one degree on the centigrade scale.*

The actual measurement of the quantity of chemical energy transformed into heat in any definite change is accomplished by the use of an apparatus called the *calorimeter*, represented in Fig. 37. The change is arranged to take place in solution in a measured volume of water contained in a thin-walled metal vessel *A*. This is placed within a double-walled vessel *B*, which contains water at the temperature of the room. The thermometer *C* indicates when the water has reached this temperature. This water is to prevent the influence of heat from without, and as an added precaution the vessel is covered with a thick layer of nonconducting felt. The heat evolved by the change raises the temperature of the solution, the rise being indicated by the thermometers *D, D*. During the change the solution is stirred by the stirrer *E*. If the weight of the water is (say) 2570 g. and the rise in temperature is 1.5° centigrade, the heat evolved is $2570 \times 1.5 = 3855$ cal.

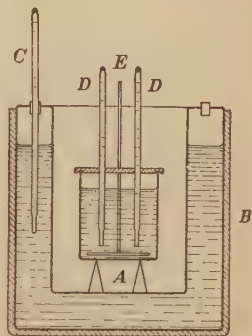


FIG. 37. A calorimeter, a form of apparatus used for determining the quantity of heat evolved in any definite chemical change

Heat changes accompanying changes in the state of water. We have stated that in the conversion of a definite weight of ice into water, or water into steam, a definite amount of heat is required. Now that we have discussed the unit of heat these facts may be stated as follows: *To convert 1 g. of ice at 0° into water at 0° requires 80 cal., while to convert 1 g. of water at 100° into steam at 100° requires 537 cal.*

Chemical energy. A body may possess energy due to its motion or to its position. A piece of coal (or of any fuel) possesses energy due neither to its motion nor to its position

but to *its ability to undergo combustion*. For in this process heat is evolved, and since heat is a form of energy, and energy cannot be created, it must be that in the process of combustion some other form of energy present in the coal and oxygen is converted into heat energy. This form of energy is called *chemical energy*. It is this form of energy in which the chemist is especially interested, for every chemical change is accompanied by a change in chemical energy, and the energy changes



FIG. 38. Formation of ozone by the action of moist air on phosphorus

are quite as important to the chemist as the changes in matter. Thus the value of any kind of coal depends primarily upon the chemical energy of the coal, for the greater the chemical energy, the greater the amount of heat that will be developed in the combustion of the coal, and it is the heat that we desire. Chemical energy, then, may be defined as *that form of energy which manifests itself when chemical action takes place*.

Ozone. It is sometimes possible to change the energy content of a substance; and by so doing we change its properties. Thus, if oxygen is subjected to the action of an electric discharge a new gas, called *ozone*, is formed which has the characteristic odor noticed about electrical machines when in operation. Ozone is simply oxygen in which the normal energy content of the oxygen is greatly increased. It is not possible to convert more than a small percentage of oxygen into ozone, since the latter gas is unstable and changes back into oxygen. A point is soon reached, therefore, when the rate of formation of ozone is just equal to the rate of its decomposition.

Ozone is a very strong oxidizing agent. Air containing ozone is sometimes used in certain manufacturing processes as well as in the purification of water.

Preparation of ozone. For commercial purposes ozone is prepared by the action of electric discharges through air. Its formation in the laboratory may be shown by partially covering with water a few pieces of stick phosphorus placed in the bottom of a jar (Fig. 38). The slow oxidation of the cold phosphorus is attended by the conversion of some oxygen into ozone. The presence of ozone in the air in the jar is soon indicated by its characteristic odor as well as by the property it possesses of imparting a blue color to strips of paper, 4, previously dipped into a solution of potassium iodide and starch.

Allotropic forms of matter. Just as oxygen and ozone are made up of the same kind of matter, so we shall find that many of the other elements occur in forms differing greatly in properties, this difference being due to their different energy contents. Such forms of matter are known as *allotropic forms*.

EXERCISES

1. Is the fact that a candle disappears on burning at variance with the law of conservation of matter?
2. The density of iron is 7.86. Compare the weight of any piece of iron with that of an equal volume of water.
3. Name some common substances that cannot be melted without decomposition.
4. Name some familiar substances that cannot be boiled without decomposition.
5. Why does not all the water in a pond freeze in winter?
6. Some people place tubs of water in their cellars in cold winters to prevent the freezing of vegetables stored in the cellars. Is such a procedure of any value?
7. Why does a block of ice melt so slowly even in warm air?
8. Why does water sprinkled on the floor cool the room?
9. Land near large volumes of water, such as the Great Lakes, is generally regarded as the best for growing fruits. Is there any reason for this belief?
10. At which place would most time be required to boil an egg hard — on the top of Pikes Peak or at Atlantic City?
11. When gases are compressed, heat is generated. Explain.

12. Name three crystalline and three amorphous substances.
13. Give three illustrations of transformation of energy in your daily experience.
14. (a) Give three ways of generating heat. (b) What is the source of the heat energy in each case?
15. Gasoline used in motor cars contains what kind of energy?
16. Name three kinds of energy purchased for use in our homes.
17. How does the energy of a compound compare with the energy of the elements present in the compound?
18. Can you suggest the source of the energy which you possess?
19. Account for the fact that sometimes rain freezes almost *instantly* when it strikes the ground or any object and thus coats it with a layer of ice.
20. How many calories of heat will be required to change 100 g. of ice at 0° into steam at 100° ?
21. 25 kg. of ice at 0° is placed in a refrigerator. Suppose that the ice melts and the temperature of the resulting water as it flows from the refrigerator is 10° . How many calories of heat have been absorbed?
22. In a certain experiment 2250 g. of water at 20° was contained in a calorimeter. After a reaction the temperature of the water was 24° . How much heat was evolved in the reaction?
23. 1 kg. of water at 20° was cooled by adding 100 g. of ice (0°) and allowed to stand until the temperature became constant. Assuming that no heat is lost in radiation, calculate the approximate temperature of the cooled water.

CHAPTER VII

COMPOUNDS OF HYDROGEN AND OXYGEN: WATER AND HYDROGEN PEROXIDE

WATER

Properties of water. Because of its great abundance and its importance to all forms of living organisms, a great deal of interest naturally attaches to hydrogen oxide, or water, as it is commonly called. Pure water is an odorless and tasteless liquid, colorless in thin layers, but having a bluish tint when observed through a considerable thickness. It solidifies at 0° and boils at 100° under the normal pressure of 1 atmosphere. When water is cooled, it steadily contracts until the temperature of 4° is reached; at lower temperatures it expands. Water is remarkable for its ability to dissolve other substances and is the most general *solvent* known. Chemists usually employ aqueous solutions of substances rather than the substances themselves, since as a rule chemical action takes place more readily in solution.

Occurrence of water. Water not only covers about five sevenths of the surface of the earth and is present in the atmosphere in the form of vapor, but it is also a common constituent of the soil, of many rocks, and of every form of animal and vegetable organism. Nearly 70 per cent of the human body is water. This is derived not only from the water which we drink but also from the food which we eat, most of which contains a large percentage of water. The table given in the chapter on foods (Chapter XXIX) shows the percentage of water present in some of the more common foods.

Historical. Water was regarded as an element until 1781, when Cavendish showed that it is formed by the union of hydrogen and oxygen. Being a believer in the phlogiston theory, however, he failed to interpret his results correctly. A few years later Lavoisier repeated Cavendish's experiments and showed that water must be regarded as a compound of hydrogen and oxygen.

Composition of natural waters. Water as it occurs in nature always contains more or less matter derived from the rocks and soils with which it comes in contact. When such water is evaporated this matter is left behind in solid form. Even rain water, which is the purest natural water, contains dust particles and gases dissolved from the atmosphere. The foreign matter in natural waters is of two kinds; namely, *mineral* and *organic*.

1. **Mineral matter.** The mineral substances ordinarily present in fresh waters are common salt and compounds of calcium, magnesium, and iron. Water containing any considerable amounts of mineral matter does not form a lather with soap, and is termed *hard water*. Water containing little or no mineral matter, such as rain water, is termed *soft water*. One liter of an average river water contains about 0.175 g. of mineral matter. The waters of the ocean contain about 40 g. of mineral matter to the liter, more than three fourths of which is common salt.

2. **Organic matter.** The organic matter present in water consists not only of the inanimate products of animal and vegetable life but also of certain living microorganisms. This matter is absorbed from the soil or introduced from sewage.

Effect of the foreign matter in water upon health. As a rule any sickness resulting from drinking impure waters is due to the presence of living microorganisms. Many of these are without injurious effect upon the human system, but some are the direct cause of disease. Thus a transmissible disease such as typhoid fever is due to a certain kind of organism

which, through food or drink, is introduced into the system. *It is easily possible for these organisms to find their way, through sewage, from persons afflicted with the disease into wells or any poorly protected water supply, and it is chiefly in this way that typhoid fever is spread.* It may be added that the appearance of a water gives no conclusive evidence as to purity. A water may be unfit for drinking and yet be clear and odorless.

The purification of water ; distilled water. Since all natural waters contain foreign matter, it is of interest to understand the methods used for removing such matter and so obtaining chemically pure water. This is best done by the process of *distillation*, which consists in boiling the water and then condensing the resulting steam. In the laboratory the process is usually conducted as follows :

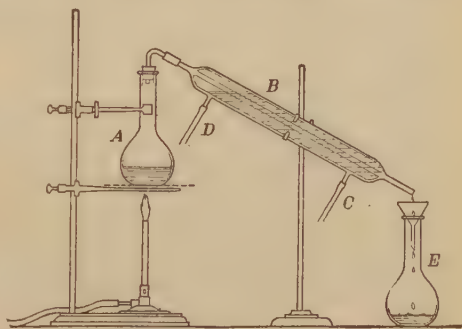


FIG. 39. The distillation of water as carried on in the laboratory

Ordinary water is poured into the flask *A* (Fig. 39) and boiled. The steam is conducted through the condenser *B*, commonly known as a Liebig condenser, which consists essentially of a narrow glass tube sealed within a larger one, the space between the two being filled with cold water, which enters at *C* and escapes at *D*. In this way the inner tube is kept cool and the steam in passing through it is liquefied. The water formed by the liquefaction of the steam collects in the receiver *E* and is known as *distilled water*. The impurities are not changed into vapor but remain in the flask *A*.

Distilled water is pure water. It is used by the chemist in almost all his work. Large quantities are also used in the manufacture of ice, as well as for drinking.

Commercial distillation. In preparing distilled water on a large scale the steam is generated in a metal boiler *A* (Fig. 40) and is conducted through the pipe *B* to the condensing coil *C*, made of tin. This pipe is wound into a spiral and is surrounded by cold water, which enters at *D* and flows out at *E*. The distilled water is collected in a suitable container *F*.

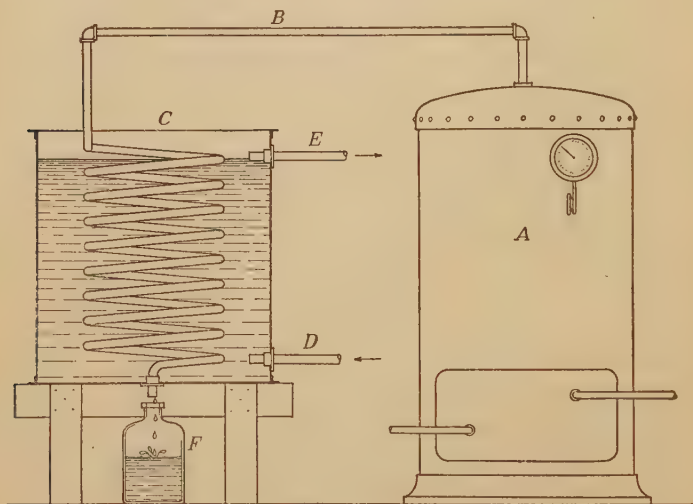


FIG. 40. The distillation of water for commercial purposes

Purification of water for sanitary purposes. When we speak of pure water, ordinarily we do not mean water from which all foreign matter has been removed but rather water which contains nothing injurious to health. All foreign matter, whether injurious or not, may be removed by distillation, but this process is costly, especially when we come to purifying large quantities of water. The method actually used for rendering water safe for drinking depends upon the volume of water to be purified.

1. *Purification of water on a small scale.* If we have any reason to doubt the purity of a water used in our homes for drinking

we can easily render it safe by simply boiling it for a few minutes. The high temperature destroys any microorganisms present. These organisms, although destroyed by heat, can withstand very low temperatures without losing their vitality.

2. *Purification of water on a large scale.* Many cities find it necessary to take their water supply from rivers and reservoirs in which the water is more or less contaminated with organic matter. Such a water supply is a source of constant menace to the health of a city.

It becomes necessary, therefore, to find some way of effectively purifying the water on a large scale. Two general methods are used for this purpose: (1) treatment with some germicide, usually chlorine

(p. 141), which destroys the microorganisms present, and (2) filtration. As a rule the two methods are combined. The water is filtered on a large scale by allowing it to drain through large filtration beds made of sand and gravel. Some of the impurities are strained out by the filter, while others are decomposed by the action of certain kinds of microorganisms which collect in a jellylike layer on the surface of the filter. Such filters are known as *slow sand filters*.

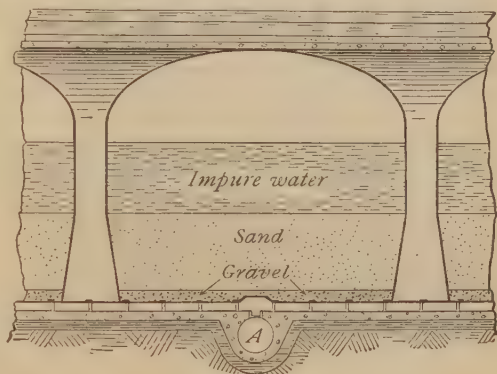


FIG. 41. A covered slow sand filter for purifying water on a large scale

Fig. 41 shows a cross section of such a filter bed. The water filters through the sand and gravel and passes into the porous pipe A, from which it is pumped into the city mains. The filters are usually covered to prevent the water from freezing.

In some cases the water before filtration is run into large tanks and treated with certain compounds, such as alum, which form in the water a small amount of jellylike substances. This slowly settles to the bottom of the tank, carrying with it much of the organic matter present. The resulting water is then filtered through a so-called mechanical filter (Fig. 42) composed of sand and gravel. This method of treatment has

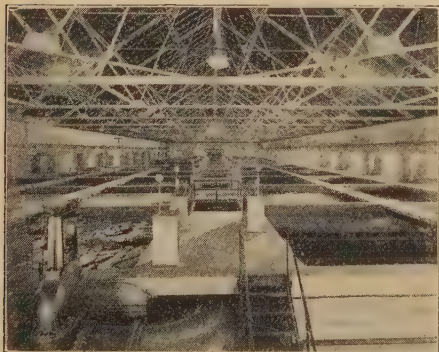


FIG. 42. Mechanical filter in a modern city filtration plant

largely replaced the slow sand filter, since the process is much more rapid and just as effective.

The effect of the filtration of the water supply upon the health of a city is shown by the fact that typhoid fever is practically unknown in a city where all the water consumed is purified by an effective

purification plant (Fig. 43). Water taken from a well in a city is always a source of danger.

Self-purification of water. It has long been known that water contaminated with organic matter tends to purify itself when exposed to the air (p. 26). This is due to the fact that air is somewhat soluble in water and that the dissolved oxygen, in the presence of certain microorganisms, gradually oxidizes the organic matter present in the water ; when this is destroyed, the organisms present die for lack of food. While water is undoubtedly purified in this way, the process cannot be relied upon to purify a contaminated water so as to render it safe for drinking purposes.

Chemical conduct. Water is a very stable substance ; in other words, it does not undergo decomposition readily. To

decompose it into its elements by heat alone requires a very high temperature. Even at 2500° only about 10 per cent of the water heated is decomposed, and on cooling the constituent gases again combine to form water. Though very stable toward heat, water can be decomposed in other ways, as by the action of the electric current or by certain metals.

Though containing 88.81 per cent of oxygen, water is not a good oxidizing agent because of its great stability. However, certain metals, as well as carbon, can be oxidized by very hot steam, the hydrogen being set free in gaseous form.

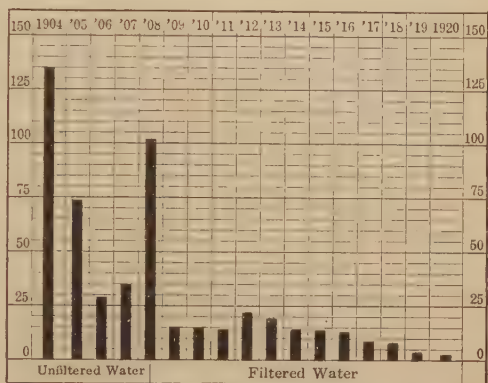


FIG. 43. This figure gives the typhoid fever death rate per 100,000 of population in Columbus, Ohio, and shows the effect of water purification in decreasing the ravages of this disease.

Water combines directly with many compounds, forming substances called *hydrates*. Blue vitriol and alum are good examples of such hydrates. A substance that contains no water whatever is said to be *anhydrous*. The term *anhydrous* literally signifies *without water*.

Heat of formation and heat of decomposition are equal. The fact that a very high temperature is necessary to decompose water into hydrogen and oxygen is in accord with the fact that a great deal of heat is evolved by the union of hydrogen and oxygen (p. 35), for it has been proved that the heat necessary to decompose (say) 1 gram of a compound into its elements (heat of decomposition) is equal to the heat evolved in the formation of 1 gram of the same compound from its elements (heat of formation).

Composition of water. We have already learned that water is composed of hydrogen and oxygen in the proportion of 11.19 per cent of hydrogen to 88.81 per cent of oxygen (p. 18). The statement has also been made that the composition of a compound can be determined only by experiment. The methods used for determining the composition of water will now be given, and the experiments will be described somewhat in detail, since they illustrate the methods used for determining the composition of compounds in general.

Methods used in determining the composition of compounds : analysis and synthesis. In general we can use either of two methods in determining the composition of a compound: (1) after finding out what elements are present in the compound we may devise a way to decompose a definite weight of it into the elements which compose it, and accurately weigh the amounts of the elements so obtained; or (2) we may measure the proportion in which the elements combine to form the compound. The former process is known as *analysis*, and this, in general, consists in *separating a substance into its component parts*; the latter is known as *synthesis*, and this consists in the *building up of a compound from its component parts*.

Each of the processes, analysis and synthesis, may be either *qualitative* or *quantitative*. Thus, qualitative analysis consists in separating a substance (either a compound or a mixture) into its component parts and finding out what these are. Quantitative analysis, on the other hand, consists in finding the weight of each component present in a definite weight of the substance.

In determining the composition of water we might naturally think that a simple method would consist in decomposing water by an electric current and measuring the relative weights of oxygen and hydrogen evolved (p. 18). This method, however, is not very accurate.

Proportion in which hydrogen and oxygen combine to form water. Experiments have already been described by which

water is proved to be a compound of hydrogen and oxygen (Figs. 19, 21). It remains for us to find out in what proportion these elements combine to form water. This may be done by mixing known volumes of hydrogen and oxygen, causing them to combine, and then ascertaining the volume and identity of the gas remaining.

Details of the experiment. The combination of the two gases is brought about in a tube called a *eudiometer*. This is a graduated glass tube about 60 cm. long and 2 cm. wide, closed at one end (Fig. 44). Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a space of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one fourth filled. The tube is then lowered until the mercury stands at the same level inside and outside the tube, and the reading of the volume of the hydrogen is taken. Approximately an equal volume of pure oxygen is then introduced, and the volume is again taken. This gives the total volume of the two gases. From this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen.

The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube is at first depressed because of the expansion of the gases due to the heat generated, but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations.

In order that the temperature of the excess gas and the mercury may become uniform, the apparatus is allowed to stand for a few

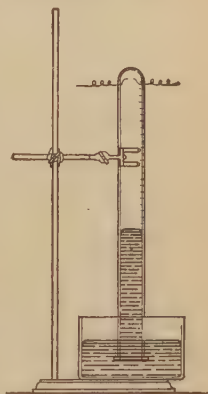


FIG. 44. The eudiometer employed in determining the composition of water

minutes and the volume of the gas is taken. The gas left over is then tested in order to ascertain whether it is hydrogen or oxygen, since experiments have proved that it is never a mixture of the two. From the information thus obtained the composition of the water may be calculated.

Calculation of composition. In an experiment carried out with great exactness in the laboratory, the readings were as follows:

Volume of hydrogen	20.3 cc.
Volume of hydrogen and oxygen	38.7 cc.
Volume of oxygen	18.4 cc.
Volume of gas left after combination has taken place (found to be oxygen)	8.3 cc.

We have thus found that 20.3 cc. of hydrogen have combined with 18.4 cc. minus 8.3 cc. (or 10.1 cc.) of oxygen, or approximately 2 volumes of hydrogen have combined with 1 volume of oxygen. Since oxygen is 15.9 times as heavy as hydrogen, the proportion by weight in which the two gases combine is 1 part of hydrogen to 7.94 parts of oxygen.

Morley's results. The American chemist Morley (Fig. 48) has determined the composition of water with greatest care. Extreme precautions were taken to use pure materials and to eliminate all sources of error. The hydrogen and oxygen which combined, as well as the water formed, were all accurately weighed. According to Morley's results 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water.

Comparison of results obtained. From the above discussion it is easy to see that it is by experiment alone that the composition of a compound can be learned. Different methods may lead to slightly different results. The more accurate the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is generally conceded by chemists that the results obtained by Morley in reference to the composition of water are the most accurate ones. In accordance with these results, then, water

must be regarded as a compound containing hydrogen and oxygen in the ratio of 1 part by weight of hydrogen to 7.94 parts by weight of oxygen.

Relation between the volume of water vapor and the volumes of hydrogen and oxygen which combine to form it. If the experiment described above (Fig. 44) is carried out at a temperature above 100° , the water vapor formed is not condensed, and it thus becomes possible to compare the volume of the water vapor with the volumes of hydrogen and oxygen which combined to form it. This can be accomplished by using a eudiometer of the shape of the letter **U** and surrounding the upper part of the eudiometer *A* (Fig. 45) with a glass tube *B*, through which is passed at *C* the vapor obtained by boiling some liquid which has a boiling point above 100° . This vapor keeps the tube *A* heated above the boiling point of water. In this way it has been proved that 2 volumes of hydrogen and 1 volume of oxygen combine to form exactly 2 volumes of water vapor. *It will be noted that the relation between these volumes may be expressed by whole numbers.* The significance of this very important fact will be discussed in a subsequent chapter.

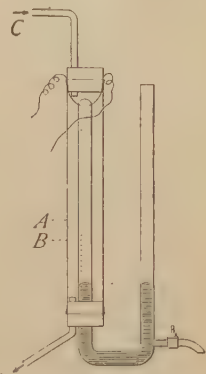


FIG. 45. Eudiometer for measuring the volume of steam formed by the union of oxygen and hydrogen

Law of definite composition. We have just seen that water contains hydrogen and oxygen combined in a perfectly definite ratio. In the earlier days of chemistry there was much discussion as to whether the composition of a given compound is always precisely the same or whether it is subject to some variation. Experiments have shown, however, that the composition of a pure chemical compound is always exactly the

same. Thus, pure water obtained from any source whatever, such as melting pure ice, condensing steam, or burning hydrogen in oxygen, always contains 1 part by weight of hydrogen to 7.94 parts of oxygen. This truth is known as the *law of definite composition* and may be stated thus: *The composition of a chemical compound never varies.*

HYDROGEN PEROXIDE

Composition. As has been shown, 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water. It is possible, however, to obtain a second compound of hydrogen and oxygen differing from water in composition in that 1 part by weight of hydrogen is combined with 2×7.94 , or 15.88, parts of oxygen. This compound is called *hydrogen peroxide*, the prefix *per-* signifying that it contains more oxygen than hydrogen oxide (water).

Properties and chemical conduct. Hydrogen peroxide is a clear, sirupy liquid whose freezing point is -1.7° . It is difficult to prepare in a pure state, since it is very unstable, decomposing into water and oxygen with explosive violence:



In dilute solution it is fairly stable, although it should be kept in a dark, cool place; otherwise the solution loses its strength, the hydrogen peroxide present gradually decomposing into water and oxygen. The presence of a small percentage of certain substances, such as a trace of acid, preserves the strength by retarding decomposition.

Uses. Solutions of hydrogen peroxide are used as oxidizing agents. The solution sold by druggists contains 97 per cent of water and 3 per cent of the peroxide. It has been largely used in medicine as an antiseptic, but recent experiments show it has little value for this purpose. It acts upon certain dyes



FIG. 46. John Dalton (English) (1766-1844)

Teacher and scientist. He developed the atomic theory and made many studies on the properties and composition of gases. His book, entitled "A New System of Chemical Philosophy," had a large influence on the development of chemistry

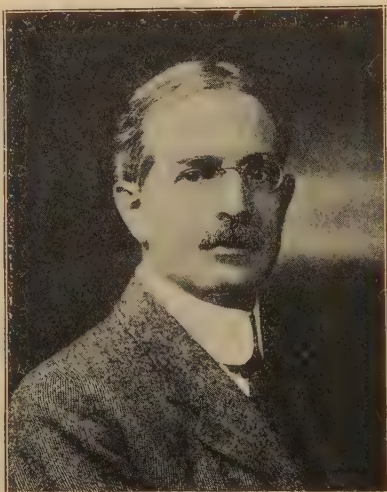


FIG. 47. Theodore William Richards (1868- .)

Professor of chemistry in Harvard University and well known for his exact investigations in many branches of chemistry. The only American chemist to receive the Nobel prize (\$40,000), which is bestowed annually upon those who have achieved greatest distinction for their contributions to knowledge



FIG. 48. Edward Williams Morley (1838-1923)

Emeritus professor of chemistry in Western Reserve University. Known for his accurate determinations of the densities of oxygen and hydrogen and of the ratio in which they combine to form water

and natural colors, such as that of the hair, oxidizing them to colorless compounds; hence it is sometimes used as a bleaching agent.

Law of multiple proportion. It has been shown that both water and hydrogen peroxide are compounds of hydrogen and oxygen and that the ratio by weight in which these two elements are present in each of these compounds is as follows:

Water	hydrogen : oxygen = 1 : 7.94
Hydrogen peroxide	hydrogen : oxygen = 1 : 15.88

It will be seen that the ratio between the weights of oxygen combined with a fixed weight of hydrogen (say 1 g.) in these two compounds is 7.94 : 15.88, or 1 : 2.

Similarly, many elements other than oxygen and hydrogen unite to form a number of distinct compounds, each with its own precise composition. In all such compounds the same statement holds as in the case of water and hydrogen peroxide—the weights of the one element which are combined with a fixed weight of the other always bear a simple ratio to each other, such as 1 : 2 or 2 : 3. This truth is known as the *law of multiple proportion*. It was formulated by John Dalton (Fig. 46) in 1808 and may be stated thus: *When any two elements, A and B, combine to form more than one compound, the weights of A which unite with any fixed weight of B bear the ratio of small whole numbers to each other.*

EXERCISES

1. What is the approximate weight of water in your body?
2. What foods have a high water content (p. 268)? What ones have a low water content?
3. In making solutions why does the chemist use distilled water rather than filtered water?
4. How could you determine the total amount of solid matter dissolved in a sample of water?
5. How could you determine whether a given sample of water is distilled water?

6. How could the presence of air dissolved in water be detected?
7. How could the amount of water in a food such as bread or potato be determined?
8. Would ice frozen from impure water necessarily be free from disease germs?
9. Why is it that merely heating water to the boiling point is not sufficient to render it safe for sanitary purposes?
10. (a) What are the advantages of using distilled water for drinking? (b) Can you suggest any possible disadvantage?
11. Mention different ways in which a well water could become contaminated.
12. What is your judgment concerning the probable purity of water taken from wells sunk in towns and cities?
13. If the water in your home town or city is purified, report on the method of purification.
14. Why is cold water passed into *C* instead of *D* in Fig. 39?
15. Mention at least two advantages that a metal condenser has over a glass condenser.
16. Draw a diagram of the apparatus used in your laboratory for supplying distilled water.
17. Suppose that the maximum density of water were at 0° instead of at 4° . What effect would this have on the formation of ice on bodies of water?
18. Compare the properties of water with the properties of the elements which compose it.
19. State the two laws given in this chapter and illustrate each with an example.
20. Distinguish between the terms *analysis* and *synthesis*; between *hydrates* and *anhydrous* substances.
21. (a) Give the characteristics of an oxidizing agent. (b) What oxidizing agents have been mentioned so far in our study?
22. Give an example of a chemical action in which the speed of the action is increased by the presence of a small amount of some definite compound; also one in which the speed is decreased.
23. 20 cc. of hydrogen and 7 cc. of oxygen are placed in a eudiometer and the mixture is exploded. What gas, and how much of it, remains in excess?

24. (a) What weight of oxygen is contained in 100 g. of water?
(b) in 100 g. of pure hydrogen peroxide?

25. From the following data determine the ratio in which oxygen and hydrogen unite, the volumes all being measured under the same conditions of temperature and pressure:

Volume of oxygen in eudiometer	8.54 cc.
Volume of oxygen and hydrogen	52.72 cc.
Volume of gas (hydrogen) left after explosion	27.10 cc.

26. Morley found the composition of water by determining the weights of hydrogen and of oxygen that combine with each other to form water. The results of two trials are as follows:

	HYDROGEN USED	OXYGEN USED
(1)	3.2645 g.	25.9176 g.
(2)	3.2559 g.	25.8531 g.

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

27. (a) What weight of water would be formed by the combustion of 100 liters of hydrogen? (b) What volume of oxygen would be required in (a)? (c) What weight of potassium chlorate is necessary to prepare this amount of oxygen?

CHAPTER VIII

NITROGEN AND THE RARE ELEMENTS ARGON, HELIUM, NEON, KRYPTON, XENON

Properties of nitrogen. We have seen that oxygen is that constituent of the atmosphere which supports life. It is a very active element, however, and we can readily imagine what would happen if the atmosphere were all oxygen. This great activity of oxygen is kept in check by the presence in the atmosphere of a large percentage of the inert gas which we call *nitrogen*, which will neither burn nor support combustion. Like oxygen and hydrogen, nitrogen is a colorless, odorless, and tasteless gas. One liter of it weighs 1.25 g. It is very slightly soluble in water, 100 cc. of water dissolving but 2.33 cc. under standard conditions. It can be obtained in the form of a colorless liquid which boils at -195.7° .

Occurrence. Dry air is composed principally of oxygen and nitrogen in the free state, about 78 parts out of every 100 parts by volume being nitrogen. Nitrogen also occurs in nature combined with potassium and oxygen in the form of potassium nitrate (commonly called *saltpeter* or *niter*); it also occurs combined with sodium and oxygen in the form of sodium nitrate. Nitrogen is likewise an essential constituent of all living organisms; it is therefore an essential constituent of our foods, being present in them in the form of *protein* (see chapter on Foods).

Historical. Nitrogen was discovered by the Scottish chemist Rutherford in 1772. A little later the Swedish chemist Scheele (Fig. 53) showed it to be a constituent of air, and Lavoisier gave it the name *azote*, which means that it will not support life. The name *nitrogen* was afterwards given to it because of its presence in *niter*.

Preparation. Nitrogen can be readily obtained either from air or by decomposition of compounds containing the element.

1. *Preparation from air.* On a large scale nitrogen is always prepared from liquid air, as will be explained in a subsequent chapter. In the laboratory it is prepared from air by the action of some substance which will combine with the oxygen, leaving the nitrogen free. Such a substance must be chosen, however, as will combine with the oxygen to form a product that is not a gas and that can be readily separated from the nitrogen. The substances most often used for this purpose are phosphorus and copper.

(a) *By the action of phosphorus.* The method used for the preparation of nitrogen by the use of phosphorus is as follows:

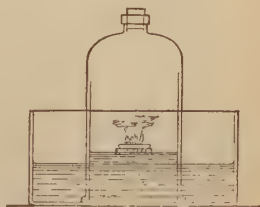


FIG. 49. Preparing nitrogen by burning out the oxygen of air with phosphorus

The phosphorus is placed in a little porcelain dish supported on a cork and floated on water (Fig. 49). It is then ignited by contact with a hot wire, and immediately a bell jar or bottle is brought over it so as to confine a portion of the air. The phosphorus combines with the oxygen to form an oxide of phosphorus known as phosphorus pentoxide. This is a white solid which floats about in the bell jar, but which in a short time is all absorbed by the water, leaving the nitrogen. As fast as the oxygen is used up the water rises in the bell jar.

(b) *By the action of copper.* The oxygen in the air may also be removed by passing air slowly through a heated tube containing copper. The copper combines with the oxygen to form copper oxide, which is a solid. The nitrogen passes on and may be collected over water. The details of the process are as follows:

The copper is placed in a tube A (Fig. 50) and heated. Air is then forced slowly through the tube by pouring water into the

bottle *B*. The oxygen of the air combines with the hot copper, forming the black solid, copper oxide, which remains in the tube, while the nitrogen passes on and is collected over water in the cylinder *C*.

2. Preparation from compounds of nitrogen. In preparing nitrogen from air, the nitrogen is never entirely pure, since it contains the rare elements argon, helium, neon, krypton, and xenon, originally present in the air. These constitute only about 1 per cent of the nitrogen and, since they resemble the

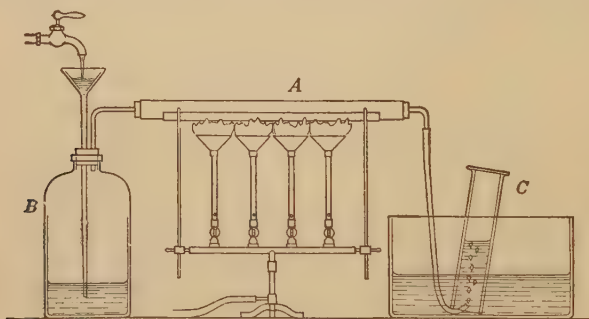


FIG. 50. Preparing nitrogen by removing the oxygen from air with hot copper

nitrogen, do not materially affect its properties. Perfectly pure nitrogen is prepared by decomposing some of its compounds.

Chemical conduct. Under ordinary conditions nitrogen is very inactive. It does not easily combine with oxygen, as is evident from the fact that the air contains both of these gases; nor does it combine with anything else very readily, as is apparent from the fact that there is so much of it in the air and so little in the earth's crust in combination with other elements.

At high temperatures the activity of nitrogen greatly increases. When it is mixed with oxygen and strongly heated a small fraction of the two gases combine, but the action is

always very incomplete. The best results are obtained by passing electric sparks through a mixture of the two gases (or air) or by causing the mixture to flow through an electric arc. Under these conditions nitric oxide is formed. Under similar conditions nitrogen and hydrogen combine to a limited extent to form the compound known as *ammonia*. When nitrogen is heated with metals the action is much more energetic, particularly with magnesium, titanium, or aluminium. The resulting compounds are called *nitrides*, just as compounds of an element with oxygen are called *oxides*.

Uses. Free nitrogen is used in the preparation of certain fertilizers. During the World War the Germans, being cut off from natural supplies of nitrates, used nitrogen in the manufacture of ammonia, and this in turn in making nitric acid, which is essential for the manufacture of explosives. The gas is also used in certain gas-filled electric lamps.

Assimilation of nitrogen by plants.

While nitrogen is an essential constituent of both plants and animals, yet with the exception of a few plants none of these organisms have the power of directly assimilating free nitrogen. For example, the nitrogen in our bodies is taken from our foods and not from the air which we breathe. It has long been known, however, that certain plants, chiefly clover, alfalfa, beans, and similar plants belonging to the botanical order *Leguminosæ*, not only thrive in poor soil but at the same time enrich it. It is now known that these plants obtain at least a portion of their nitrogen from the atmosphere. This is accomplished by groups of microorganisms which are gathered in little tubercles on the roots of the plants (Fig. 51). These organisms really constitute the workers in little chemical



FIG. 51. Tubercles on the roots of bean plants

factories located on the roots of the plants and in which the nitrogen of the air is converted into compounds of nitrogen; some of these compounds are assimilated by the plant and some are left in the soil and thus enrich it (Fig. 52).



FIG. 52. A field of alfalfa

One of nature's factories for the assimilation of nitrogen

Argon, helium, neon, krypton, xenon. These are rare gaseous elements and occur in the air in very small quantities. They are similar in that they are all colorless, odorless gases. They differ from all other known elements in that they are entirely inactive, forming no compounds whatever. Argon, the most abundant of the group, was discovered in 1894 by two British scientists, Lord Rayleigh and Sir William Ramsay (Fig. 54).

It is now prepared from

liquid air and, like nitrogen, used in certain gas-filled electric lamps. In 1868 Lockyer showed that a gaseous element, to which he gave the name *helium*, was present in the gases surrounding the sun. In 1895 Ramsay showed that this same element was present in the gases evolved in heating certain rare minerals and that traces were present in the atmosphere. Later Cady found it in the natural gas issuing from certain wells in Kansas and Texas. It is the most difficult of all gases to liquefy, having a boiling point of -268.7° . The three remaining members of the group were discovered by Ramsay and Travers in 1898. They obtained them from liquid air, thus proving their presence in the atmosphere. Tubes containing neon are used to detect faulty automobile spark plugs.

FIG. 53. Karl Wilhelm
Scheele (1742-1786)

This Swedish chemist was one of the greatest experimenters of his century. He discovered oxygen independently of Priestley, as well as the elements chlorine, tungsten, and molybdenum. He prepared the deadly gases arsine and prussic acid. He first isolated many organic compounds, such as glycerin and oxalic, tartaric, and citric acids. Scheele was one of the ablest as well as one of the latest defenders of the phlogiston theory of combustion



FIG. 54. Sir William Ramsay
(1852-1916)

An English chemist, who, together with the English scientist Lord Rayleigh, discovered argon. In association with Travers he also discovered the elements xenon, neon, and krypton and was the first to show that helium exists on the earth. For these and other outstanding discoveries, Ramsay was awarded the Nobel prize in 1904



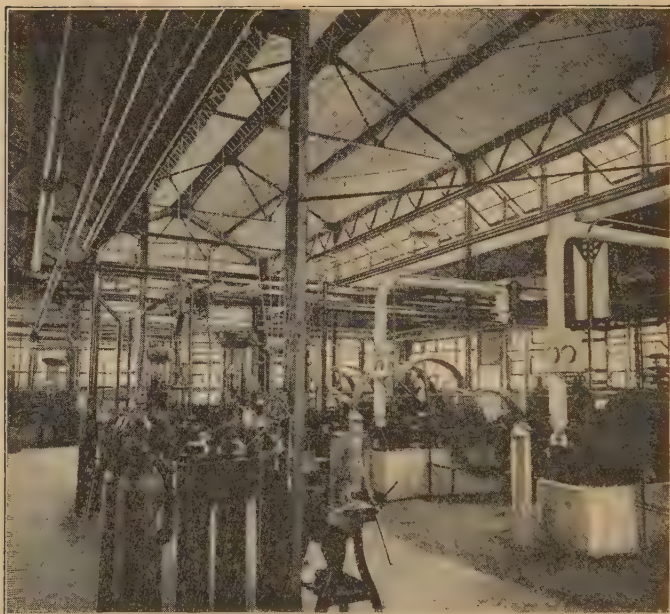


FIG. 55. An interior view of one of the plants built at Fort Worth, Texas, for the separation of helium from natural gas

Until the year 1918 helium had been obtained in minute quantities only. When the United States entered the World War an effort was made to find some noncombustible gas for filling observation balloons, since the records showed that 95 per cent of the casualties resulting from the use of such balloons was due to the highly combustible character of the hydrogen with which they were filled. Helium was the only gas that at all met the requirements. An effort was made, therefore, to obtain it from the natural gas found in certain localities in Texas, which contained about 1 per cent of helium. To separate the helium, advantage was taken of its very low boiling point. The problem was exceedingly difficult. When the armistice was signed, however, 147,000 cu. ft. of nearly pure helium, stored in steel cylinders, was on its way to our armies, and the gas, which at the beginning of the war was almost a chemical curiosity and cost about \$1700 per cubic foot, was being prepared in quantities at a cost of 10 cents per cubic foot. At the close of the war the government constructed at Fort Worth, Texas, a large plant for the separation of the helium from the natural gas of that locality. The first dirigible inflated with helium encircled the Capitol at Washington, December, 1921

TABLE OF RARE ATMOSPHERIC ELEMENTS

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 liter . . .	0.1782 g.	0.9002 g.	1.7809 g.	3.708 g.	5.851 g.
Boiling point of liquid form	- 268.7°	- 239°	- 186°	- 151.7°	- 109°
Number of volumes in 1,000,000 volumes of air (approximate) . .	4.00	12.3	9400	0.05	0.006

EXERCISES

1. Contrast the properties and chemical conduct of oxygen, hydrogen, and nitrogen.
2. In what connections has Scheele's name been mentioned?
3. Calculate the relative weights of nitrogen and oxygen; of nitrogen and hydrogen.
4. In preparing nitrogen from the air why not use a burning candle for removing the oxygen?
5. In Fig. 49 why does the water rise in the jar? Does this suggest a way for determining the percentage of oxygen in the air?
6. Compare the solubilities of oxygen, hydrogen, and nitrogen in water.
7. Do plants really assimilate free nitrogen?
8. Why is alfalfa regarded as such an important crop in agriculture?
9. State the significance of each of the following names: argon, helium, neon, krypton, xenon, nitrogen. (Consult dictionary.)
10. In what respect do the rare elements in the atmosphere differ from nitrogen and all other elements?
11. (a) 100 liters of dry air contains how many liters of nitrogen?
(b) What is the weight of this volume of nitrogen?
12. In an experiment 50 liters of dry air was passed over hot copper (Fig. 50). (a) What volume of nitrogen was obtained? (b) How much did the copper increase in weight?
13. A student prepared 25 liters of nitrogen collected over water in a laboratory in which the thermometer registered 20° and the barometer 742 mm. Calculate the volume of this nitrogen under standard conditions.

CHAPTER IX

MOLECULAR WEIGHTS; ATOMIC WEIGHTS

Molecules. We have seen that the way gases act, as described in the gas laws, proves beyond any doubt that every gas is made up of extremely small particles called *molecules*. Methods have been found for actually calculating the weights of the individual molecules with considerable accuracy, but these weights are so small that we can make little practical use of them. To help us realize how small the molecules are Langmuir has calculated that if the molecules in one cubic inch of air were to be each one changed into a grain of fine sea sand, the resulting sand would fill a trench a mile wide and three feet deep, reaching from New York to San Francisco.

Atoms. A moment's reflection will show that the molecule of a *compound*, such as water, must be made up of different parts, for a compound contains at least two different elements, and so each molecule of the compound must have some of each constituent. *These constituent parts of a molecule are called atoms.* The law of definite composition states the fact that the composition of any sample of a compound is always the same. Consequently each molecule of the compound must consist of the same number and kind of atoms. If the law is true, then it follows that the atoms of any given element must either have the same weight, or if they are slightly different in weight the mixture must always average the same. Later on we shall see that some elements consist of atoms of different weights but always in the same ratio.

The atomic theory. It was this striking law of definite composition that led John Dalton (Fig. 46) in 1806 to advance the theory that each elementary body is made up of a vast number of individual atoms, and this suggestion was called the *atomic theory*. We now have such convincing evidence that this picture of the make-up of matter is a true one that we accept it as a truth rather than as a theory, *for any theory becomes a truth when there is no longer any doubt as to its reality.*

Relative molecular weights. It will be recalled (p. 47) that the simplicity of the gas laws led Avogadro to believe that equal volumes of any two gases inclose the same number of molecules, no matter what their size or weight may be. So many additional facts are now known that there can be no doubt that Avogadro's principle is a statement of the truth. We can even determine the number of molecules in a cubic centimeter of air with more precision than we can take the census of a large city.

With the help of Avogadro's principle we can at once determine the *relative* weights of the molecules of various gaseous substances. For in any definite volume — say 1 liter — there will always be the same number of molecules no matter what gas fills the liter measure. So the weights of the different liters will be in the *same ratio* as those of the several kinds of molecules constituting the gases.

Thus a liter of oxygen weighs 1.429 g., a liter of hydrogen weighs 0.08987 g., and one of nitrogen weighs 1.2507 g. These figures give the actual weight in grams of *equal numbers* of the three kinds of molecules. They must therefore be in the *same ratio to each other* as the actual weights of the three kinds of molecules.

Relative atomic weights. The next question is, Have we any simple way for determining the *relative weights of the atoms* that constitute the molecules? At first sight it might appear that the law of definite composition affords us such a method.

Taking water as an example, we know that each portion we analyze consists of 1 part of hydrogen to 7.94 parts of oxygen *by weight*. Therefore the composition of each *molecule* must be expressed by this ratio. If the molecules were all made up of one atom each of oxygen and hydrogen, then these two numbers, 1 and 7.94, would be the relative weights of the atoms, and our problem would be solved. *These numbers that state the ratio by weight in which two elements combine are called the combining weights of the elements*, and they can be determined with great precision by the analysis of compounds.

But there is another compound of hydrogen with oxygen, namely, hydrogen peroxide, and in this the ratio is 1 : 15.88 (p. 73), so that oxygen and hydrogen have *two* combining weights. Here our trouble begins, for we have no direct way to tell which of these two compounds (if either of them) is the one that has one atom of each element in its molecules. It is evident, however, that in all such cases *the one combining ratio (or combining weight) must be a simple multiple of the other*, for the atoms will have to combine in some definite small ratio, such as 1 : 1 or 1 : 2. This fact at once shows the reason for the law of multiple proportion.

We have now made real progress in determining the relative weights of the atoms, for we can determine the ratio by weight of two elements in the compounds they form with each other (the combining weights), and *some one of these combining weights must be the atomic weight*. Years of effort to solve the problem completely have shown that we must follow an unexpected plan. We must first get the *molecular weights of compounds* of the elements and from these draw conclusions as to the *relative weights of the constituent atoms*.

Standard for molecular weights. When we have to deal with any series of purely relative values, such as molecular weights, we usually choose some one as unity and express the others in terms of this one. For example, in our coinage we may select

the dollar as our standard and state the value of the other coins as fractions and multiples of this; or we may select the penny and state the value of all others as multiples of this. We may select the dime and call it 10 or 25 or any number we choose, and calculate the value of all other coins to the standard we have selected. Whatever coin we select and whatever value we give it, the *ratio* in value between all the coins will remain unchanged.

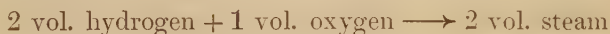
In a similar way we might call oxygen unity. The ratio by weight between the liter of oxygen, hydrogen, and nitrogen would then be $1 : 0.0629 : 0.875$. But in general we should like to avoid numbers that are less than unity, just as we have avoided coining a halfpenny, so we might take the liter of the smallest weight (hydrogen) as unity, and the ratios would then be $15.88 : 1 : 13.9$. *Since oxygen plays such an important part in chemistry we should like to stick to it as our standard*, while keeping the weights of all other molecules above unity. We can therefore provisionally adopt the round number 16 for oxygen, and the ratio becomes $16 : 1.008 : 14.01$.

By determining the weight of one liter of each of all known gases we can decide upon the relative weights of their molecules referred to this standard (oxygen = 16) or any standard we may later adopt.

Standard for atomic weights. Since the molecules are made up of atoms, and we are going to find a way to determine the relative weights of the *atoms* as well as those of the *molecules*, it is important to adopt a final standard for molecular weights that will be suitable for both molecules and atoms. Thus, if it were to turn out that the molecules of oxygen gas and hydrogen gas are not single atoms, *but are each made up of two atoms*, then the standard of 16 for the oxygen molecule would give us 8 for the oxygen atom and 0.5 for the hydrogen atom, and it would be better to adopt 32 for the oxygen molecule so as to have the hydrogen atom at least 1.

Two atoms in the oxygen molecule. It is clear that if molecules of compounds consist of two or more atoms, the molecule of elementary gases, such as oxygen or hydrogen, may either be single atoms or they may be composed of two or more atoms of the same kind. That the molecules of both oxygen and hydrogen consist of two atoms can be shown as follows:

When oxygen and hydrogen combine to form steam we have the volume relations shown in the equation (p. 71)



Let us suppose that the 1 volume of oxygen contains 100 molecules. Then the 2 volumes of steam must contain 200 molecules (Avogadro's principle). But each of these 200 molecules must contain *at least* one atom of oxygen, or 200 in all, and these 200 atoms came from 100 molecules of oxygen. Therefore each molecule of oxygen must contain *at least* two atoms. Similar reasoning shows that the molecule of hydrogen also must contain at least two atoms.

Evidently we have merely shown that there are *at least* two atoms in these molecules. There might be more than that, but there is no evidence that points this way, and we assume that there are two only. To retain the value 16 for the *atom* of oxygen (and a little above unity for that of hydrogen) we will now adopt oxygen as 32 as the final standard for molecular and atomic weights and compare all others with this value.

Molecular weights from the weight of 22.4 liters. Having adopted the arbitrary value oxygen = 32 as our standard, let us calculate the volume occupied by 32 g. of oxygen gas. Since 1 liter weighs 1.429 g. the volume occupied by 32 g. will be $\frac{32}{1.429}$, or 22.4 liters. If we make a vessel that holds exactly 22.4 liters and fill it with oxygen, it will hold the standard molecular weight (measured in grams); namely, 32 g. If

we now replace the oxygen with nitrogen, the same number of molecules will be present as before (Avogadro's principle), and experiment shows that the weight is 28.02. But these two numbers, 32 and 28.02, are the relative weights of an equal number of molecules, so that the nitrogen molecule weighs 28.02 compared with the oxygen molecule as 32. In like manner the weight of 22.4 liters of *any* gas will give its molecular

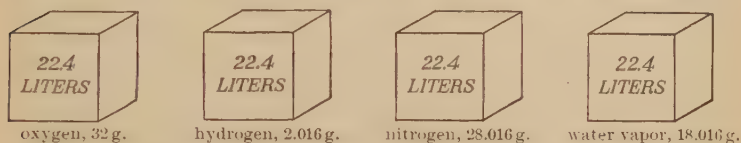


FIG. 56. The weight of 22.4 l. of various gases

weight referred to oxygen as 32 (Fig. 56), and we can say that *the number which expresses the weight of 22.4 liters of any gas is the same as the number which expresses the molecular weight of the gas.*

Remarks. Very few of the gases expand and contract *exactly* as the gas laws say they should. Consequently the weight of 22.4 liters of a gas is not its *exact* molecular weight, but is within a few tenths of one per cent of it.

Evidently the method we have found applies merely to gases (including liquids and solids that can be converted into gases). In an elementary course we cannot take up any other cases, and we need only say that methods are known for determining the molecular weights of liquids and of dissolved solids.

Selection of the atomic weight from the combining weights.

It will now be easy to show how we can decide which one of the combining weights of an element is really its atomic weight, and the best way to do this is by an example. So let us suppose that we have found that the combining weights of nitrogen are 7.005, 14.01, and 21.015; the atomic weight is, therefore, one of these numbers.

We first determine the weight of 22.4 liters of a number of gaseous compounds which we know to contain nitrogen. These values are given in the first column of the following table :

GASEOUS COMPOUNDS	MOLECULAR WEIGHT (22.4 LITERS)	PERCENTAGE OF NITROGEN BY EXPERIMENT	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas	27.95	100.00	27.95
Nitrous oxide	44.13	63.70	28.11
Nitric oxide	30.00	46.74	14.02
Ammonia	17.05	82.28	14.03

We next analyze each of these compounds to ascertain the percentage of nitrogen present, placing the values obtained in the second column. If we multiply the molecular weight of each compound by the percentage of nitrogen, *the product will be the portion of the molecular weight due to nitrogen*. But since the molecules are made up of *atoms*, the part of a molecule due to nitrogen must represent the *sum of the weights of the nitrogen atoms present*. We notice that the numbers in the last column are either very near to 14 or to twice 14 and that none are near 7 or 21. If we examine a large number of nitrogen compounds, it is reasonable to expect that we should find some that contain only one atom, and since we find none which give a value of less than 14, we assume that this and not 7 or 21 or 28 represents the weight of a nitrogen atom.

Accurate determination of atomic weights. The weight of a given volume of a gas is difficult to determine with great precision, and in consequence the molecular weights of gases as determined by experiment are usually subject to a very considerable error. The portion of nitrogen in 22.4 liters of the various gases is therefore a little uncertain, as will be seen from the values in the table above. All these figures tell us is that the true value is *very near 14*. The *combining weight* can be very accurately determined by the analysis of any of

these compounds, and is found to be 7.005. It is therefore evident that the *accurate* atomic weight is twice this value; namely, 14.01.

Summary. These, then, are the steps which must be taken to establish the atomic weight of an element:

1. Determine the combining weight accurately by analysis.
2. Determine the weight of 22.4 liters of a large number of gaseous compounds of the element and, by analysis, the part of the molecular weights due to the element. *The smallest number so obtained will be the approximate atomic weight.*

3. Multiply the combining weight by the integer (1, 2, or 3), which will give a number close to the approximate atomic weight. *The number so obtained will be the precise atomic weight.*

Molecular weights of the elements. When we determine the weight of 22.4 liters of the various *elementary* gases we reach some interesting conclusions. Experiment shows that the molecular weights of many of them, such as nitrogen, chlorine, and bromine, give values which are *twice the atomic weights*, so that in these cases the molecule contains two atoms, as we have found to be true with oxygen and hydrogen (p. 86). In the case of the metals, so far as their vapors have been studied, the molecular weight and the atomic weight are the same, *so that the molecule of a metal must consist of a single atom.* The molecule of ozone, on the other hand, contains three atoms of oxygen, while the molecules of phosphorus and arsenic contain four atoms.

Weight of a liter of gas. The weight of 1 liter of each gas is determined by actually weighing the gas, and from this weight we calculate the molecular weight of the gas. Conversely, if we happen to know the molecular weight of the gas, we can easily calculate back to the weight of 1 liter of the gas, for the number which represents the molecular weight also represents the weight of 22.4 liters of the gas. Hence, to find the weight of 1 liter of any gas divide its molecular weight by 22.4.

EXERCISES

1. Is it correct to speak (*a*) of an atom of a compound? (*b*) of a molecule of an element?

2. State the law upon which is based our method for determining molecular weights.

3. Almost every one of us uses the word *theory*. What do we mean by the term?

4. Is a theory an expression of truth? If not, what is the distinction?

5. Mention a theory that has been discarded because proved false (p. 20), also one that has become a truth.

6. (*a*) Mention the reasons why oxygen is selected as a standard for atomic and molecular weights rather than hydrogen, which is the lightest of all elements. (*b*) Why not represent oxygen as 1 rather than 16 as the standard for atomic weights?

7. Calculate the relative weights of the molecules (*a*) of hydrogen and oxygen (see Appendix for weights of 1 liter of various gases); (*b*) of hydrogen and nitrogen.

8. Calculate the molecular weights of hydrogen, oxygen, and hydrogen chloride from the weight of 1 liter of each of these gases (Appendix).

9. Carbon dioxide is one of the gases exhaled from our lungs. Calculate its molecular weight from the weight of 1 liter of the gas.

10. When sulfur burns in oxygen or air (p. 20) a gas known as *sulfur dioxide* forms. The molecular weight of sulfur dioxide is 64.06. (*a*) Calculate the weight of 1 liter of the gas. (*b*) Compare your result with that given in the Appendix.

11. The chief constituent of natural gas is a compound of carbon and hydrogen known as *methane*. Its molecular weight is 16.04. (*a*) Calculate the weight of 1 liter of the gas. (*b*) Compare your result with that given in the Appendix.

12. Sulfur dioxide contains 50.05 per cent of sulfur. One liter of the gas weighs 2.9266 g. Assuming that the molecule of the sulfur dioxide contains but one atom of sulfur, calculate the atomic weight of sulfur from the above data. (*Suggestion*. First calculate the molecular weight of the gas; then determine how much of this weight is sulfur.)

13. Carbon dioxide (see exercise 9, above) contains 72.72 per cent of oxygen. Assuming that the molecule of the gas contains two atoms of oxygen, calculate the atomic weight of oxygen.

CHAPTER X

FORMULAS; EQUATIONS; SOLUTION OF PROBLEMS

Percentage composition. Just as we can determine the composition of water with great accuracy (p. 68), so, by similar means, we can determine the composition of other compounds. Having analyzed a given compound, we usually express its composition in percentages, or in the parts of each element in 100 parts of the compound. Thus, we have seen that water consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen. This mode of expression takes no account of the fact that compounds are made up of molecules, the atoms of which each have characteristic weights. It would be much better to have a method of stating composition which will express all these facts.

Atomic composition. Remembering that the atomic weight of oxygen is 16, it is evident that if we divide the percentage of oxygen in water by 16, the quotient (5.55) will be the *relative number of oxygen atoms in 100 parts of water*. In like manner, if we divide the percentage of hydrogen (11.19) by the atomic weight of the element (1.008), the quotient (11.10) will express the *relative number of hydrogen atoms in 100 parts of water*. The two numbers, 5.55 and 11.10, therefore represent the *ratio between the number of oxygen and hydrogen atoms in 100 g. of water*. But *this same ratio must hold for any other quantity of water, even for one molecule, since any quantity of water is made up of molecules*. To reduce the ratio to its simplest terms we divide the two numbers by the smaller one:

$$5.55 \div 5.55 = 1; 11.10 \div 5.55 = 2$$

The ratio of oxygen atoms to hydrogen atoms in a molecule of water is therefore 1:2.

Formulas. We may express the ratio found for the oxygen and hydrogen atoms in a molecule of water by writing the two symbols together thus, H_2O , the subscript 2 indicating that two atoms of hydrogen are in combination with one of oxygen. The ratio of oxygen atoms to hydrogen atoms (namely, 1:2) could, however, be just as well represented by any multiple of H_2O , such as H_4O_2 or H_6O_3 , for in all these the ratio of the oxygen to hydrogen atoms is the same. We must therefore decide, if possible, which of these expresses the true composition of the molecule of water. Now it is very easy to do this if we know the molecular weight of water, for if H_2O is right, then the molecular weight of water must be equal to 2 times the atomic weight of hydrogen ($2 \times 1.008 = 2.016$) + the atomic weight of oxygen (16), or 18.016. If H_4O_2 is correct, then the molecular weight will be 2×18.016 , or 36.032. Now, it is possible by Avogadro's principle to determine the molecular weight of water vapor, and in this way it is found to be approximately 18. Hence H_2O correctly represents the composition of the molecule of water as vapor. The expression H_2O is termed the *formula* of water. It may then be stated in general that *the formula of a compound or element is an expression which represents the composition of the molecule of the compound or element in terms of atoms.*

Derivation of the formula of potassium chlorate. Let us take another example. Potassium chlorate when analyzed in the laboratory is found to be as follows: potassium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. Now, proceeding as in the case of water, we get the following results:

$$31.9 \div 39.10 = 0.8158 = \text{relative number of atoms of K in 100 g.}$$

$$28.9 \div 35.46 = 0.8150 = \text{relative number of atoms of Cl in 100 g.}$$

$$39.2 \div 16.00 = 2.4500 = \text{relative number of atoms of O in 100 g.}$$

Dividing the three quotients by the smallest (0.8150) we get the integers 1, 1, 3. (Since analyses are always slightly inaccurate, the ratios found will often differ slightly from whole numbers, but

the difference is so slight as to leave no doubt as to what the integer really is.) The simplest formula of potassium chlorate is therefore KClO_3 , and its real formula is either KClO_3 or some multiple of this. If KClO_3 is correct, then its molecular weight is $(39.10 + 35.46 + 3 \times 16)$, or 122.56. Experiments show that the molecular weight is approximately 122; hence KClO_3 is the correct formula.

Calculation of the molecular weight and the percentage composition of compounds. We have seen that it is possible to determine the percentage composition of a compound and its molecular weight by experiment, and knowing these we can calculate the formula of the compound. On the other hand, *having once determined the formula* of a compound and knowing the atomic weights of the elements present in it (see Appendix), we can easily calculate back to the molecular weight and the percentage composition from which the formula was derived; and it is sometimes convenient to do this, for it is easier to remember formulas than percentage composition. For example, knowing that the formula of water is H_2O , its molecular weight must be the sum of two atomic weights of hydrogen (2×1.008) and one atomic weight of oxygen (16), or 18.016. Now if the molecule of water weighs 18.016 and contains one atom of oxygen weighing 16, then $16/18.016$, or 88.81 per cent, of the water is oxygen, and $2.016/18.016$, or 11.19 per cent, must be hydrogen.

Let us take another example; namely, hydrogen sulfate. Its formula is H_2SO_4 ; hence its molecular weight is the sum of 2 times the atomic weight of hydrogen (2×1.008) plus the atomic weight of sulfur (32.06) + 4 times the atomic weight of oxygen (4×16), or 98.076.

$$\text{Percentage of hydrogen} = \frac{2.016}{98.076} = 2.05$$

$$\text{Percentage of sulfur} = \frac{32.06}{98.076} = 32.70$$

$$\text{Percentage of oxygen} = \frac{64}{98.076} = 65.25$$

Gram-molecular weights. For practical purposes we deal with pounds or with grams of a substance, not with atoms and molecules. Now, since the numbers 18.016, 16, and 2.016 represent the ratio by weight between a molecule of water and the oxygen and hydrogen of which it is composed, the same ratios must hold between any weight of water we may choose and the oxygen and hydrogen in this weight of water. Evidently in 18.016 lb. of water there will be 16 lb. of oxygen and 2.016 lb. of hydrogen, and in 18.016 g. there will be 16 g. of oxygen and 2.016 g. of hydrogen.

For practical purposes, therefore, we may allow the symbol H to stand for 1.008 g. of hydrogen, the symbol O for 16 g. of oxygen, and the formula H_2O for 18.016 g. of water. The weight in grams of an element, corresponding to its atomic weight, is called a *gram-atomic weight*. The weight in grams of an element or of a compound, corresponding to its molecular weight, is called a *gram-molecular weight*.

Equations. Having devised a convenient way of expressing the composition of compounds, not in percentages but in formulas, we make use of *equations* to express chemical transformations, using an arrow in place of an equality sign. For example, the equation



is a concise method of stating two distinct facts.

1. *Qualitatively*, it states that water is formed by the union of hydrogen and oxygen.

2. *Quantitatively*, it tells us that 2 gram-atomic weights of hydrogen (2.016 g.) combine with 1 gram-atomic weight of oxygen (16 g.) to form 1 gram-molecular weight of water (18.016 g.).

Molecular equations. Since a formula expresses the composition of a molecule, and since experiment has shown that a molecule of oxygen and one of hydrogen each contain two

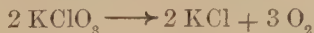
atoms, the formulas of these gases are written O_2 and H_2 rather than $2 O$ or $2 H$, which would simply represent two atoms not combined. If we wish our equation to state these additional facts, we shall have to change it to the form



This is called a *molecular equation*, and it will be seen that it expresses the same ratios by weight as does equation (1). It also expresses the fact that 2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water, and this for some purposes makes it a more useful equation. In this text we shall ordinarily use the molecular equations, although we may sometimes use the simple form if we wish only to express ratios.

While the molecules of hydrogen and oxygen are made up of two atoms each, this is not the case with all elements. Thus the phosphorus molecule contains four atoms, and we write it P_4 . *In the case of some elements, especially the metals, the molecule contains but one atom; in such cases, therefore, the atom and the molecule are identical.*

Decomposition of potassium chlorate. Let us take another example of the meaning of an equation. It will be remembered that oxygen was prepared by heating potassium chlorate, which has the formula $KClO_3$. When heated, this compound decomposes into oxygen and a compound called potassium chloride whose formula is KCl . The decomposition is represented by the equation



This equation states the following facts:

1. *Qualitatively*, potassium chlorate decomposes into potassium chloride and oxygen.

2. *Quantitatively*, 2 gram-molecular weights of potassium chlorate (2×122.6 g.) decompose into 2 gram-molecular weights of potassium chloride (2×74.56 g.) and 3 gram-molecular weights of oxygen (3×32 g.). The number before a formula applies to the

formula as a whole, while the subscript number applies only to the symbol which it follows.

3. *Molecularly*, 2 molecules of potassium chlorate decompose into 2 molecules of potassium chloride and 3 of oxygen.

Steps in writing an equation. *We must keep in mind that chemical equations simply express facts deduced from experiments.* In other words, we cannot find out by equation-writing what the formula of a compound is or what changes the compound undergoes, but having found out these facts we can express them by an equation. In writing an equation the first step consists in writing the formulas (or symbols) of the substances entering into the reaction on the left of the arrow ($\longrightarrow$), and on the right the formulas (or symbols) of the substances formed. Thus, having learned that the formula of mercuric oxide is HgO , that it decomposes on heating into mercury and oxygen, and that the oxygen molecule is O_2 , while the mercury atoms remain single, we express these facts as follows:

First step: $\text{HgO} \longrightarrow \text{Hg} + \text{O}_2$

The second and final step consists in *balancing the equation*; that is, we must modify our equation (if necessary) so that there will be just as many atoms of each element on one side of the equation as on the other. Thus, in the above equation we have two atoms of oxygen (or 1 molecule) on one side of the equation. To get this we must take 2 HgO , and this will give us 2 Hg as well as O_2 ; hence we write the completed equation, keeping in mind also that the molecules and atoms of metals are as a rule identical (p. 95):

Second step: $2 \text{HgO} \longrightarrow 2 \text{Hg} + \text{O}_2$

Equations of reactions so far studied. Let us now put into the form of equations the reactions studied up to this point, writing both steps. *Remember that the complete equation in each case is the correct one; the first is written simply as an aid in formulating the completed equation.*

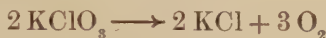
1. *Preparation of oxygen :*

(a) From potassium chlorate :

First step,

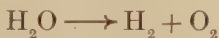


Complete,

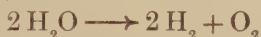


(b) From the electrolysis of water :

First step,



Complete,

2. *Preparation of hydrogen :*

(a) From sodium and water :

First step,

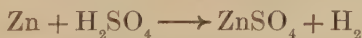


Complete,



(b) From zinc and sulfuric acid :

First step and complete (identical),



(c) From zinc and hydrochloric acid :

First step,



Complete,



(d) From iron and steam :

First step,



Complete,



Representation of the heat of reaction. We can also employ chemical equations to express the heat given off or absorbed during chemical action. The equation



states the fact that when 4.032 g. of hydrogen combines with 32 g. of oxygen, forming 36.032 g. of water, heat is given off to the extent of 136,800 cal. Evidently when 1 gram-molecular weight (18.016 g.) of water is formed, 68,400 cal. is given off, and this is called the *heat of formation* of water.

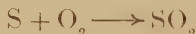
Conditions of a reaction not indicated by equations. Equations merely state the composition of the substances taking part in the reaction and the weights of each one involved, together with the energy change measured as heat. They do not tell the conditions under which the reaction will take place. For example, the equation



does not tell us that it is necessary to keep heating the mercuric oxide at a moderately high temperature in order to effect its decomposition. The equation



in no way indicates that the hydrogen sulfate must be dissolved in water before it will act upon zinc. The equation



does not indicate that no perceptible action takes place unless the sulfur is first heated, but that when once started it goes on of its own accord and with a bright flame.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

Problems based on equations. Since an equation is a statement of the weights of materials which take part in a reaction,

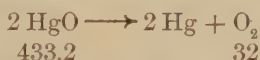
when the equation has once been established by experiment we can use it in calculating the various weights. A few examples will show how this may be done.

1. How many grams of oxygen are evolved on heating 100 g. of mercuric oxide?

First write the equation for the reaction involved:

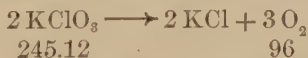


Next determine the *relative* weights of the amounts of the different substances involved in the reaction. The atomic weights of mercury and oxygen are respectively 200.6 and 16 (see table on back cover). Hence the relative weight of the 2 HgO equals $2(200.6 + 16)$, or 433.2. Similarly, the relative weight of the oxygen evolved, namely, O_2 , equals 2×16 , or 32. It is convenient now to write these numbers under the formulas in equation (1). This then becomes



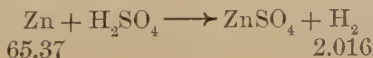
These numbers indicate that 433.2 units by weight (in this case grams) of mercuric oxide will, on heating, evolve 32 units by weight of oxygen: hence 1 g. of mercuric oxide will give $\frac{32}{433.2}$ g. of oxygen, and 100 g. will give $100 \times \frac{32}{433.2}$, or 7.38 g.

2. I wish to prepare 100 g. of oxygen, using potassium chlorate as a source of the oxygen. How many grams of the chlorate will be required?



The figures tell us that 245.12 g. of potassium chlorate will yield 96 g. of oxygen; hence to prepare 1 g. of oxygen we must use $\frac{245.12}{96}$ g. of potassium chlorate, and to prepare 100 g. we must have $\frac{245.12}{96} \times 100 = 255.33$ g.

3. How many grams of zinc must be dissolved in sulfuric acid to produce 10 g. of hydrogen?

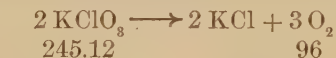


To obtain 2.016 g. of hydrogen we must use 65.37 g. of zinc. Hence to obtain 1 g. of hydrogen, $\frac{65.37}{2.016}$ g. of zinc is required, and to obtain 10 g. we must take 10 times as much; namely, $\frac{65.37}{2.016} \times 10 = 324.25$.

It must be remembered that the equations show relations by *weight*, not by volume; hence in problems involving volumes of gases it will be necessary first to find the weights of the gases. The table in the Appendix gives the weight of 1 liter of each of the common gases, measured under standard conditions. The following problem will illustrate the method:

4. How many grams of potassium chlorate are necessary to prepare 100 liters of oxygen?

Since 1 liter of oxygen weighs 1.429 g., 100 liters will weigh 142.9 g.



$$\frac{245.12}{96} \times 142.9 = 364.86 \text{ g.}$$

It will be recalled that in Chapters III and IV we have solved a number of problems of the same kind as those solved above, but in the earlier chapters these problems were solved by referring to the percentage composition of the compounds. Having now learned the significance of formulas and equations, it is much simpler to solve problems of this kind by reference to the formulas and equations involved in the problem.

In working out such problems do not carry divisions beyond the second decimal place. Having completed a problem, look to see if the result is reasonable.

EXERCISES

1. State all the facts expressed by the formula H_2O ; by H_2SO_4 .
2. State all the facts expressed by the equation



3. A compound analyzed in the laboratory was found to contain 2.76 per cent hydrogen and 97.24 per cent chlorine. Its molecular weight was found to be approximately 36. Calculate its formula.

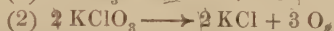
4. Common salt has a molecular weight of approximately 58 and contains 39.34 per cent sodium and 60.65 per cent chlorine. Calculate its formula.

5. Ordinary saltpeter has a molecular weight of approximately 101 and contains 38.67 per cent potassium, 13.88 per cent nitrogen, and 47.45 per cent oxygen. Calculate its formula.

6. A compound has the following composition: hydrogen, 5.92 per cent; oxygen, 94.07 per cent. Its molecular weight is approximately 34. What is the compound?

7. (a) Hydrogen sulfate has the formula H_2SO_4 . Calculate its molecular weight and its percentage composition from its formula. (b) Compare your results with those given on page 33.

8. (a) Do both of the following equations balance?



(b) What additional facts does the second one express?

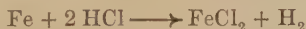
9. Balance the following equations:



10. Suppose you wish to prepare 80 g. of oxygen by heating potassium chlorate: (a) write the equation involved in the reaction; (b) from the equation calculate the weight of potassium chlorate that will be required.

11. A student added to 100 g. of zinc sufficient sulfuric acid to dissolve it. (a) Write the equation for the reaction involved; (b) calculate the weight of hydrogen evolved; (c) calculate the volume of the hydrogen.

12. When iron is dissolved in hydrochloric acid, hydrogen is evolved, as expressed in the equation



Suppose you wish to prepare 100 liters of hydrogen by this method.

(a) What would this volume of hydrogen weigh? (b) What weight of iron would be necessary to prepare this weight of hydrogen?

13. A student heated 25 g. of potassium chlorate in a flask until all the oxygen was evolved. (a) Calculate the volume of the oxygen given off. (b) What weight of potassium chloride remained in the flask?

CHAPTER XI

CARBON AND ITS OXIDES

Introduction. The term *carbon* is more or less familiar to everyone. It suggests coal and smoke and troubles with automobile engines. In the cities, especially, it annoys us by soiling our clothes. Not so many persons, however, realize that this soft black substance which is so useful as a fuel has also its artistic value, for it is the same substance which composes the very hard, brilliant gem prized for centuries and known as the diamond. Carbon also occurs in other forms, and before studying its properties we must first learn what some of these forms are.

Occurrence. In the uncombined state carbon is found in nature in several forms. The *diamond* is practically pure carbon, while *graphite* and the various forms of *coal* all contain more or less free carbon. The element also occurs abundantly in the form of compounds. Carbon dioxide, which we breathe from our lungs, is its most familiar gaseous compound. Natural gas and petroleum are largely compounds of carbon and hydrogen. It is a constituent of limestone, as well as of many other rocks. All living organisms, both plant and animal (p. 10), contain a large percentage of this element, and the number of its compounds which go to make up the vast variety of animate nature is almost limitless. In the free state carbon occurs in both the crystalline and the amorphous form.

Crystalline carbon. Crystalline carbon occurs in two forms; namely, diamond and graphite.

1. *Diamond.* Diamonds are found in certain localities in South Africa, the East Indies, and Brazil. The crystals as found are usually covered with a rough coating. These are cut so as to bring out the brilliancy of the gem. Diamond-cutting is carried on very extensively in Holland.

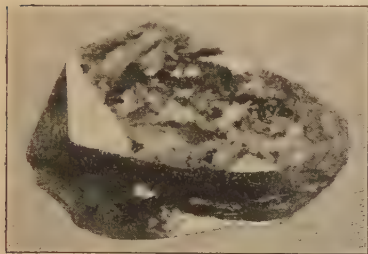


FIG. 57. The largest diamond ever found, the famous Cullinan diamond, in its original condition (one half natural size)

Fig. 57 is a photograph of the largest diamond ever found, in its original condition. It is known as the Cullinan diamond and was presented to King Edward VII by the Transvaal government. Fig. 58

is a photograph (natural size) of another very famous diamond (the Kohinoor), in finished form.

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it; but when heated in oxygen or the air, it blackens and burns, forming carbon dioxide.

Preparation of artificial diamonds.

Many attempts have been made to produce diamonds artificially. For a long time these ended in failure, graphite and not diamonds being the product obtained, but in 1893 the French chemist Moissan (Fig. 112), in his study of chemistry at high temperatures, finally succeeded in making some small ones. He accomplished this by dissolving carbon in melted iron and plunging the crucible containing the mixture into water, as shown in Fig. 59. Under these conditions the carbon crystallized in the iron in the form of the diamond. The

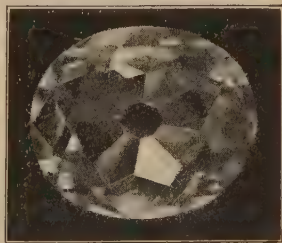


FIG. 58. The Kohinoor diamond after being cut (natural size)

crystals were then freed from the metal by dissolving away the iron in hydrochloric acid. The resulting diamonds were too small to be of any use.

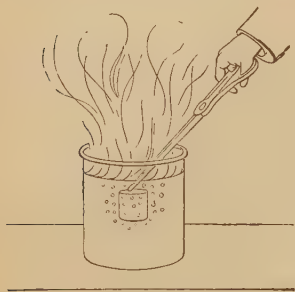


FIG. 59. Sketch illustrating Moissan's method of producing diamonds in the laboratory

2. Graphite. This form of carbon is found in large quantities, especially in Ceylon, Siberia, and in some parts of the United States, Mexico, and Canada. Large quantities are also made commercially by heating hard coal to a high temperature. It is a shining black substance, very soft, and greasy to the touch. Its density is about 2.15. It is used in the manufacture of lead pencils and crucibles,

as a lubricant, and (in the form of a polish or a paint) as a protective covering for iron.

Commercial production of graphite. The process consists in heating hard coal in large electric furnaces about 40 ft. in length, a longitudinal section of one of which is shown in Fig. 60. The electrodes *A* are made of graphite. The furnace is nearly filled with

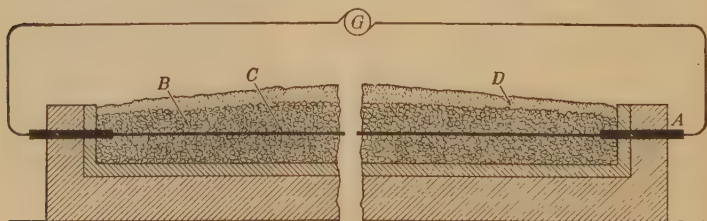


FIG. 60. Electric furnace for the production of graphite

the coarse grains of coal *B*. Since the coal is a poor conductor of electricity, there is placed in the center of the charge a core, *C*, of carbon, which serves to carry the current through the charge. The charge is covered with a mixture, *D*, of sand and carbon

(or similar materials), which serves to exclude the air. An electric current is supplied by the generator *G*. The current in passing through the charge meets with resistance sufficient to produce a high temperature. Under the influence of the intense heat the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit and is therefore superior to the natural product for most purposes.



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FIG. 61. Mining coal in a typical mine

Amorphous carbon. Pure amorphous carbon is best prepared by heating sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in the absence of air. The hydrogen and oxygen present are expelled, largely in the form of water, and pure carbon remains. Almost any form of organic matter yields carbon when heated in the absence of air. Among the numerous substances that contain amorphous carbon, the following may be mentioned:

1. **Coal and coke.** The various forms of coal (Fig. 61) were formed from vast accumulations of vegetable matter. In *hard* coal, or *anthracite*, nearly all the carbon present is in the uncombined state; while in *soft*, or *bituminous*, coal a considerable

portion of the carbon present is combined with hydrogen, oxygen, nitrogen, and sulfur. When soft coal is heated in the absence of air complex changes occur (as will be described in a later chapter), resulting in the formation of various useful compounds of carbon, which are given off in the form of gases and vapors, while the mineral matter and free carbon remain and constitute ordinary *coke*. The matter which escapes when

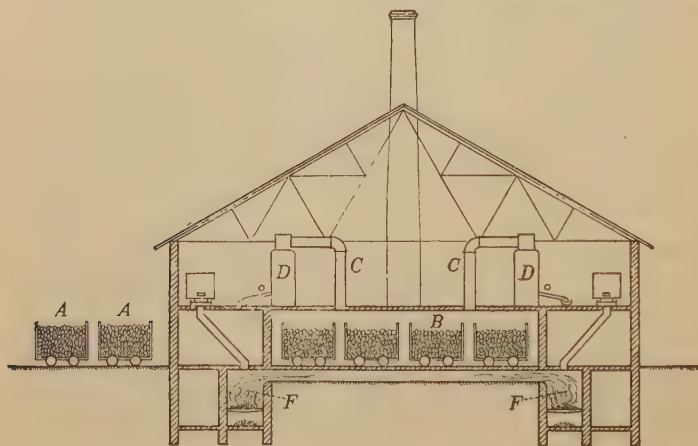


FIG. 62. Drawing of a plant for the production of charcoal by the modern method

coal is heated in the absence of air is known as *volatile matter*. In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left in the form of *ash*.

2. **Charcoal.** This is prepared from wood just as coke is prepared from coal. The volatile matter formed and expelled by the heat contains many valuable substances, such as *wood alcohol* and *acetic acid*, which are obtained commercially in this way. Formerly much of this volatile matter was allowed to escape, but at present a large amount of charcoal is prepared

in such a way that the volatile matter is condensed and saved, as in the heating of coal for making coke. Both charcoal and coke are used as fuels and are especially useful in reducing metals from their oxides, as will be explained later.

Modern methods for the production of charcoal. Iron cars are loaded with wood *A, A* (Fig. 62) and run into a low, narrow iron room, or *retort B*. The retort is then made air-tight and heated slowly for twenty-four hours by the fires *F, F*. The volatile products escape through the pipes *C, C* and then pass into the condensers *D, D*. Here those portions which are liquid at ordinary temperatures, such as *wood alcohol* and *acetic acid*, are condensed, while the gaseous products are led back and burned in the fires *F, F*. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood.

3. Boneblack, or animal charcoal. This is made by charring bones and animal refuse. It consists of very finely divided carbon and of calcium phosphate and is especially useful for removing coloring matter in the refining of sugar.

4. Carbonblack; lampblack. The black powders known as carbonblack and lampblack are products of the imperfect combustion of carbonaceous fuels, such as oil and gas.

Destructive distillation. The process of heating a substance such as coal, wood, and bones, in the absence of air, is known as *destructive distillation*. Thus we say that charcoal is prepared by the destructive distillation of wood. This process differs from ordinary distillation in that complex changes occur, resulting in the formation of new compounds.

Properties of carbon. While the various forms of carbon differ in many properties, especially in hardness, yet they are all odorless, tasteless solids, insoluble in water, and characterized by their stability toward heat. Even when subjected to the intense heat of the electric arc, carbon does not melt, though it vaporizes to some extent.

In the form of boneblack carbon withdraws certain kinds of organic matter from solutions; hence its use in refining sugar and other substances. A marked property of carbon is its ability to take up (or, in chemical terms, to *adsorb*) large volumes of gases. The amount of gas adsorbed by any given sample of carbon



FIG. 63. A form of gas mask used in the World War as a protection against poison gas

depends not only on the material from which the carbon is prepared but also on the method of preparation. That prepared from coconut shells and peach seeds is one of the best for this purpose. Thus, one volume of charcoal prepared from coconut shells will adsorb about 250 volumes of air and about 335 of chlorine, a gaseous element used so largely as a poison gas in the World War. Charcoal prepared especially for adsorbing gases is known as *activated charcoal*.

Gas masks. The use of various poison gases such as phosgene (p. 26) in the World War made it necessary to devise gas masks for the protection of the troops. Many different kind of masks were used, but as finally developed, these were made and fitted to the face (Fig. 63) in such a way that all the inhaled air had to pass through a light metal box (canister) filled with layers of various materials, the chief of which was activated charcoal. These materials either adsorbed or combined with the poison gases. They were so efficient that poison gas present in the ratio of 1000 parts of gas to 1,000,000 of air could be reduced to one part per million in the small fraction of a second required for the air to pass through the canister.

Chemical conduct. At ordinary temperatures carbon is a very inert substance, but at higher temperatures it combines directly with most of the elements. Because of its strong affinity for oxygen it is an excellent reducing agent. Its compounds with the metals are called *carbides*. One of the most important of these is *calcium carbide* (CaC_2), which is used in the preparation of acetylene. When carbon or a substance containing it, such as wood or coal, burns, the element combines with oxygen to form either *carbon dioxide* (CO_2) or *carbon monoxide* (CO). Both of these oxides are colorless gases.

Uses of carbon. The chief use of amorphous carbon is for fuel to furnish heat and power for all the uses of civilization. An enormous quantity of carbon in the form of coal, coke, and charcoal is used as a reducing agent in the separation of the various metals from their ores. Carbonblack is used for making motor-car tires, indelible ink, printer's ink, paints, and black varnishes, while boneblack and charcoal are used in filters. In the refining of sugar the dark solution of the impure compound is filtered through boneblack, which removes the coloring matter. On evaporation the resulting solution yields the colorless sugar. Activated charcoal is used in refining various products and in making gas masks for protecting workmen in certain industries from the evil effects of poisonous gas evolved in industrial operations.

How the chemist determines the percentage of carbon in a sample of coal. To determine the percentage of carbon in a sample of coal the chemist weighs out a small amount of the sample, say 1 g., in a narrow dish *A* (Fig. 64) and slips it into the glass tube *B*, arranged so that it can be heated in the furnace, as shown in the figure. The remaining part of the tube is filled with some oxidizing agent, usually copper oxide. The glass tube is then gradually heated to a red heat, while a slow current of air, dried and free from carbon dioxide, is passed into the tube at *C*. Under these conditions the carbon in the coal burns to carbon dioxide. This gas then passes through the narrow tube *D* into the tube *E*,

filled with calcium chloride, which absorbs any water present. The carbon dioxide passes on into *F* and there bubbles through a solution of some substance, such as sodium hydroxide, and is

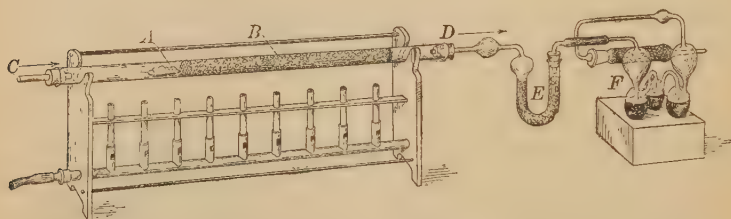


FIG. 64. Apparatus for determining the percentage of carbon in coal

absorbed. The increase in the weight of the tube *F* (and contents) gives the weight of the carbon dioxide formed. From this weight of carbon dioxide the weight of carbon present in it is easily calculated, and this equals the weight of carbon present in the 1 g. of coal burned.

Carbon dioxide (carbonic acid gas): properties and occurrence. Carbon dioxide, often known as *carbonic acid gas*, is a colorless and practically odorless gas which is exhaled from our lungs and is formed whenever any of the common fuels (all of which contain carbon) burn in oxygen or air.

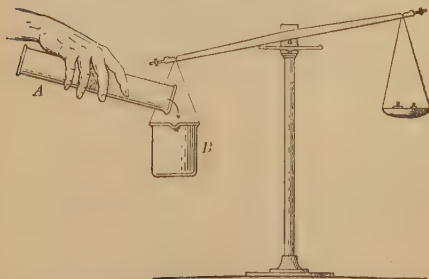


FIG. 65. A method for showing that carbon dioxide is a heavy gas



Large quantities also escape from volcanoes and crevices in the earth.

It is present in the open air to the extent of about 3 parts in 10,000. When we study the atmosphere we shall see that this relatively small amount is essential to the life of all plants.

Carbon dioxide is one of the heaviest of gases, 1 liter weighing 1.9768 g. Its weight may be inferred from the fact that it can be poured like water from one vessel downward into another; or, as a more striking experiment, the gas may be poured from a cylinder *A* into a beaker *B* attached to a balance and counterpoised as shown in Fig. 65. At 15° and under ordinary pressure 1 volume of water dissolves 1 volume of the gas. It is rather easily condensed to a colorless solid, which, under ordinary pressure, evaporates without melting at -78.5° . The gas is not regarded as poisonous, although life is not possible in an atmosphere containing large percentages of it.

Liquid and solid carbon dioxide.

The commercial carbon dioxide compressed in steel cylinders is under such great pressure that it is largely in the liquid state. When the pressure is removed the rapid vaporization of the liquid reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid (Fig. 66). Cylinders of liquid carbon dioxide are inexpensive and should be available in every school. It is possible to separate the carbon dioxide formed in the combustion of coal from the other gases formed at the same time, and this constitutes the chief commercial source of the gas.

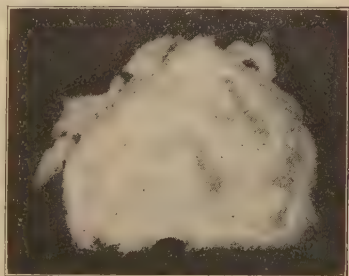


FIG. 66. Carbon dioxide in the solid form

To prepare the solid carbon dioxide the cylinder should be placed across the table and supported in such a way that the stopcock end is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth around the neck of the stopcock. The stopcock is then turned on so that the liquid rushes out in large quantities. A considerable quantity of the snow very quickly collects in the cloth.

Preparation. In the laboratory carbon dioxide is prepared by the action of hydrochloric acid on the compound known as

calcium carbonate (CaCO_3). The latter is found in nature in many different substances, such as shells, coral, and limestone. Marble is nearly pure calcium carbonate and is the material most often used in the preparation of carbon dioxide. When hydrochloric acid and marble are brought in contact with each other, water, calcium chloride (CaCl_2), and carbon dioxide are formed according to the following equation :



With sulfuric acid the products are calcium sulfate (CaSO_4), water, and carbon dioxide.

In the preparation of carbon dioxide pieces of marble are placed in the flask *A* (Fig. 67). Hydrochloric acid is added drop by drop through the funnel tube *B*. The carbon dioxide escapes through *C* and, being heavier than air, collects in the cylinder, as shown in the figure. The calcium chloride formed is a white solid which remains dissolved in the water in *A*.

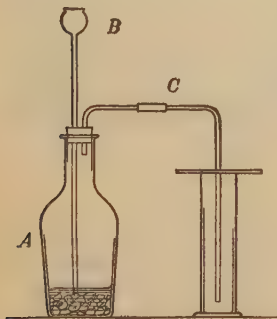


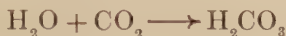
FIG. 67. A simple apparatus for preparing carbon dioxide by the action of hydrochloric acid on marble

Chemical conduct. Carbon dioxide is a very stable substance. It is neither combustible nor a supporter of combustion. When it is passed into a clear solution of calcium hydroxide, CaO_2H_2 (ordinary *lime-water*), the solution soon becomes cloudy, owing to the formation of calcium carbonate. The calcium carbonate (CaCO_3) is insoluble and separates as a solid as fast as it is formed, producing a cloudy or milky appearance in the solution :



These properties constitute a simple test for carbon dioxide.

When passed into water a portion of the gas unites with the water, forming a very unstable compound (H_2CO_3) known as *carbonic acid*. Thus:



Uses. The carbon dioxide in the air is a food for plants, as will be shown in the chapter on the atmosphere. Commercially it is used chiefly in the manufacture of soda water and similar beverages and as a fire extinguisher. Ordinary soda water consists of various flavoring extracts to which is added water charged with carbon dioxide under pressure. When the pressure is removed, the excess of gas escapes, producing *effervescence*. A burning candle is extinguished in air which contains as little as 2.5 per cent of carbon dioxide, hence the dioxide is used as a fire extinguisher.

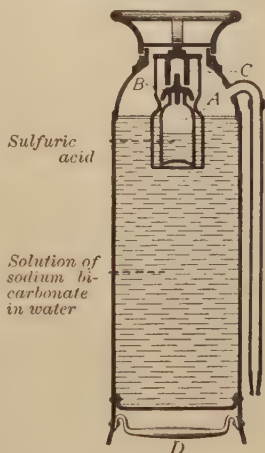


FIG. 68. A modern fire extinguisher in which water and carbon dioxide are used to extinguish the flame

Portable fire extinguishers. Familiar types of portable fire extinguishers are shown in Figs. 68, 69. That shown in Fig. 68 is a device for generating carbon dioxide under pressure. The liquid is a solution of sodium bicarbonate in water contained in a metal cylinder. The bottle *A* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *D* and the apparatus inverted. The stopper *B*, resting on the top of the bottle *A*, drops down onto the support *C*. The acid flows slowly from the bottle and at once reacts with the sodium bicarbonate, generating carbon dioxide. Some of the gas dissolves in the water, while the rest forces the water out through the nozzle. While the volume of water so obtained is not large, it is very effective as a fire extinguisher because of the carbon

dioxide accompanying it. The type of extinguisher shown in Fig. 69 is a smaller metal cylinder filled with the liquid known as carbon tetrachloride (CCl_4) and fitted with a sort of piston for forcing the liquid out in case of fire. The liquid is not combustible and is quite volatile; hence when it is thrown onto a fire it volatilizes and, the vapor being heavy, surrounds the burning body and prevents the oxygen of the air from coming in contact with it.



FIG. 69. A fire extinguisher for spraying carbon tetrachloride on a flame

Carbon monoxide (CO). This compound resembles carbon dioxide in that it is a colorless, nearly odorless gas. It differs from it in being very inflammable as well as very poisonous.

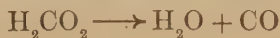
It is interesting to note that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril.

Carbon monoxide gas is formed whenever carbon is burned in a limited supply of oxygen:

$$2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$$

It is often formed in stoves when the air draft is shut off, especially when hard coal is used as a fuel. Since the gas is very poisonous, care should be taken that the pipes and chimneys are not closed in any way; otherwise the gas may escape into the room and cause the death of those inhaling it. The gas is formed in the combustion of gasoline in engines, especially if the carburetor is not well adjusted, and a number of cases of poisoning have resulted from breathing the air in closed garages in which an engine is allowed to run.

In the laboratory the gas is usually prepared by heating *formic acid* (H_2CO_2) or *oxalic acid* ($\text{H}_2\text{C}_2\text{O}_4$) with sulfuric acid, which is added to absorb the water formed:



Chemical conduct. Chemically carbon monoxide is quite active. It combines readily with oxygen and burns in air with a characteristic pale-blue flame (often observed in the combustion of hard coal), forming carbon dioxide:



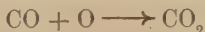
It reduces metallic oxides such as copper oxide (CuO), forming the metal and carbon dioxide



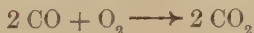
Because of this property carbon monoxide is often used as a reducing agent in liberating the metals from their oxides. It combines with chlorine to form *phosgene* (COCl_2), a very poisonous, colorless gas used largely in the World War as a poison gas.

Solution of problems. We have seen that a gram-molecular weight of any pure gas is the weight of 22.4 liters of the gas expressed in grams. By keeping this in mind it is possible for us to calculate in a very simple way the volume relations of gases entering into a reaction. All that we have to do is to write the equation so that each gas is represented in a molecular state. The number of gram-molecules of each gas entering into the reaction when multiplied by 22.4 gives the volume of the gas. The following problem will make the method clear:

What volume of oxygen is required to burn 100 liters of carbon monoxide? First write the simple equation for the reaction:



This, however, represents but 1 atom of oxygen; hence it must be doubled so as to represent a molecule of oxygen (O_2):



This equation tells us that 2 gram-molecules of carbon monoxide, or 44.8 liters (2×22.4), will combine with 1 gram-molecule of oxygen, or 22.4 liters. In other words, 2 liters of carbon monoxide will combine with 1 liter of oxygen; hence 100 liters of carbon monoxide will combine with 50 liters of oxygen.

EXERCISES

1. Suggest a method for proving that all the various forms of carbon described are really carbon.
2. How could you determine the relative percentages of carbon in different samples of coal?
3. To what is the black color of the letters on this page due?
4. Why does sugar turn black when heated?
5. Why is the end of a telegraph pole often painted with carbon paint before placing it in the ground?
6. How does carbon differ from the other elements so far studied?
7. Is there any relation between the value of different samples of coal and the ash which they form when burned?
8. How does boneblack differ in composition from carbonblack?
9. Would charcoal used in a gas mask ever lose its effectiveness?
10. Contrast the properties of the two oxides of carbon.
11. Why is carbon monoxide regarded as a treacherous poison?
12. How could you distinguish between oxygen, hydrogen, carbon dioxide, and carbon monoxide?
13. When carbon monoxide acts as a reducing agent what change does it undergo?
14. Why are different methods used for collecting oxygen and carbon dioxide when they are prepared in the laboratory?
15. Carbon dioxide sometimes collects in deep wells. How could you prove its presence in such cases?
16. What are the sources of the carbon and the oxygen in the carbon dioxide which we breathe from our lungs?
17. Carbon dioxide contains a large percentage of oxygen, but it is not an oxidizing agent. Explain.
18. Wood alcohol and acetic acid (as well as many other compounds) are obtained when certain kinds of wood are heated in the absence of air. Does this imply that these compounds are present in wood?
19. How do we account for the widely different properties of the diamond and coal?
20. What is the percentage of carbon (*a*) in carbon dioxide? (*b*) in carbon monoxide?

21. (a) Calculate the weight of oxygen combined with 1 g. of carbon in carbon dioxide. (*Suggestion.* First write the equation for the formation of carbon dioxide and then proceed as explained in the paragraph entitled "Problems based on Equations," p. 98). (b) Calculate the weight of oxygen combined with 1 g. of carbon in carbon monoxide. Are the results obtained in (a) and (b) in accord with the law of multiple proportion?

22. The average person exhales about 8 liters of air per minute containing about 4 per cent of carbon dioxide by volume. Calculate the number of liters of carbon dioxide exhaled in twenty-four hours by such a person.

23. 100 kg. of coal containing 85 per cent of carbon is burned. (a) What weight of carbon dioxide is produced? (b) What volume will this occupy under standard conditions?

24. Suppose you wish to fill a tank holding 50 liters with carbon dioxide. (a) What weight of marble will be required for its preparation? (b) What weight of hydrogen chloride will be needed?

25. What volume of carbon dioxide will be formed in the combustion of 100 liters of carbon monoxide? (*Suggestion.* Note that both of the compounds involved are gases; write the molecular equation and solve by inspection.)

26. 1 g. of coal on combustion gave 3 g. of carbon dioxide. (a) What is the weight of the carbon in the 3 g. of carbon dioxide? (b) What is the source of this carbon? (c) Calculate the percentage of carbon in the sample of coal burned.

CHAPTER XII

VALENCE

Valence of elements. If we note carefully the formulas of the compounds given in the previous chapter, it will be seen that the atoms of the various elements differ among themselves in respect to the number of other atoms with which they combine. Taking into account for the present only those formulas that contain two kinds of atoms, we see that one atom of chlorine combines with one atom of hydrogen as shown by the formula HCl , while one atom of oxygen combines with two of hydrogen (H_2O). Later we shall find that one atom of nitrogen combines with three atoms of hydrogen (NH_3), while one atom of carbon combines with four of hydrogen (CH_4). Moreover, when sodium acts on water we have seen (p. 97) that one atom of sodium displaces one of hydrogen; on the other hand, when zinc acts on sulfuric acid one atom of the metal displaces two of hydrogen (p. 97).

These observations bring into view an important property of the atoms called *valence*. *The valence of an atom is that property which determines how many atoms of any other kind it can hold in combination or can displace in a reaction.*

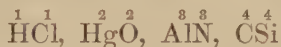
Standard of valence. Since the atoms of neither hydrogen nor chlorine combine with more than one atom of another kind (to form a compound which contains only two kinds of atoms), they are called *univalent* atoms and serve as a standard for the valence of other atoms. Oxygen, sulfur, iron, and zinc, whose atoms combine with two of hydrogen or of chlorine, are called *bivalent*. There are other elements whose atoms have

still higher valences, of three (tervalent), four (quadrivalent), and so on up to a valence of eight.

From all that has been said it might be inferred that in the compound CuO the atoms both of copper and of oxygen are univalent, because there is one of each in the molecule of copper oxide. But measured by hydrogen, oxygen is bivalent (H_2O). As we shall see below, copper must be bivalent also. We must always keep in mind that oxygen is bivalent when we deduce the valence of an element from the formula of its oxide.

Applications of valence. While it is not possible at this point to go very far into the subject of valence, the following general principles will be of service:

1. If two elements which have the same valence combine to form a compound, they will combine atom for atom, as shown in the following formulas, in which the valence of the atom of each element is designated by the figure above the symbol:



2. If two elements which have different valences combine to form a compound, then such numbers of atoms of the two elements will combine as will add up an equal number of valences, thus:



Hydrogen is univalent, while oxygen is bivalent, as is expressed by the figures over the formula of water. There is 1 atom of oxygen (2 valences); hence there must be a sufficient number of hydrogen atoms to add up 2 valences; namely, 2 atoms.

Again, in the formula CO_2 the carbon is quadrivalent. Hence, for each atom of carbon (4 valences) there must be 2 atoms of oxygen (4 valences).

3. In any reaction in which one element takes the place of another in a compound, or one in which one element of a compound exchanges places with an element in another compound,

the exchange must be between such numbers of atoms of the two elements involved as will add up an equal number of valences; for example, one atom of a bivalent element will displace two atoms of a univalent element, while two atoms of a trivalent element (6 valences) will displace three atoms of a bivalent element (6 valences).



With very few exceptions the elements do not have a single fixed valence. Most of them have two valences and some have more. Thus mercury forms the compounds HgCl and HgCl_2 , in which the mercury is univalent in the one and bivalent in the other. Similarly, compounds represented by the formulas SnCl_2 and SnCl_4 are formed by tin. Moreover, an element often has one valence for one kind of an element and a different valence for another. Thus sulfur is bivalent in the compound H_2S , but quadrivalent in the compound SO_2 .

Precautions in the use of valence. While the general idea of valence is often of great assistance, yet it must be added that the student will meet with many cases which (at first sight at least) are misleading. Thus, in the formula for hydrogen peroxide, H_2O_2 , one would be inclined to say that hydrogen and oxygen have the same valence; while the formula for iron oxide, Fe_3O_4 , would indicate that the iron has a valence of $2\frac{2}{3}$, which is an absurdity. It is not possible in an elementary book to go into detail in all these cases, but some of them will be explained in later chapters.

Table of valences. The usual valences of the elements will become familiar as we study formulas of their compounds. In

the following table, however, are given the usual valences of a few of the most important elements.

VALENCE OF ELEMENTS

Univalent	H, Na, K, Ag, Cl, Br, I
Bivalent	Ca, Ba, Mg, Zn, Hg, Fe, S, O
Tervalent	Al, Bi, As, Sb, Fe, N, P
Quadrivalent	Sn, C, Si, S
Quinivalent	N, P, As, Sb

EXERCISES

NOTE. To find the symbols for the various elements consult the table of the elements.

1. Assuming that hydrogen is always univalent and oxygen always bivalent, state the valence of each of the elements in the following compounds:



2. In the common oxide of arsenic, the arsenic is trivalent. What is the formula of the oxide?

3. Antimony (tervalent) combines directly with sulfur (bivalent). What is the formula of the resulting compound?

4. Iron (bivalent) reacts with both hydrochloric and sulfuric acids, displacing the hydrogen. Write the equation for each of the reactions.

5. Aluminium (tervalent) reacts with hydrochloric acid, displacing the hydrogen. Write the equation for the reaction.

6. Complete and balance the following equation, in which the hydrogen and mercury (bivalent) exchange places:



7. Phosphorus forms two different compounds with chlorine, in which the phosphorus is respectively trivalent and quinivalent. What is the formula of each of the compounds?

8. Phosphorus forms two different compounds with oxygen, in which the phosphorus is respectively trivalent and quinivalent. What is the formula of each of the compounds?

CHAPTER XIII

THE AIR

Introduction. The words *atmosphere* and *air* are often used interchangeably, although, strictly speaking, the former is applied to the entire gaseous envelope surrounding the earth, while the latter is applied to a limited portion, such as the air of a room. Like water, air was formerly regarded as an element. Near the close of the eighteenth century, however, through the experiments of Scheele, Priestley, Cavendish, and Lavoisier, it was shown to be a mixture of at least two gases — those which we now call oxygen and nitrogen. By absorbing the oxygen from an inclosed volume of air and measuring the contraction in volume due to the removal of oxygen, Cavendish was able to determine with considerable accuracy the relative volumes of oxygen and nitrogen present.

Inasmuch as air is composed principally of a mixture of oxygen and nitrogen, elements which have already been described, its properties may be inferred largely from those of the two gases. One liter weighs 1.2928 g.

Composition of the air. The normal constituents of air, together with the approximate volumes of each in samples collected in the open fields, are as follows:

Oxygen	21 volumes in 100 volumes of dry air
Nitrogen	78 volumes in 100 volumes of dry air
Water vapor	variable within wide limits
Carbon dioxide	3 to 4 volumes in 10,000 volumes of dry air
Argon	0.940 volumes in 100 volumes of dry air
Helium, neon	traces
Krypton, xenon	traces

In addition there are usually present small quantities of hydrogen peroxide, ammonium nitrate, microorganisms, dust particles, and traces of hydrogen. Although not definitely proved, it is probable that small amounts of ozone are also present. The air in large cities and manufacturing districts is also likely to contain certain gases evolved in manufacturing processes. Among these are hydrogen sulfide (H_2S) and sulfur dioxide (SO_2).

Water vapor in the air. The quantity of water vapor which may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cu. m. of air can absorb at the temperature indicated:

Temperature,	0°	10°	20°	30°
Weight of water,	4.8 g.	9.9 g.	17.1 g.	30 g.

Constituents of the air that are essential to life. The constituents that are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide. The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. It is likewise assimilated by certain plants (p. 79). The water vapor prevents excessive evaporation of the water present in organisms, while the carbon dioxide is an essential plant food.

Quantitative analysis of air. A number of different methods have been devised for the determination of the percentages of the constituents of the atmosphere. Among these are the following:

1. **Determination of oxygen.** The oxygen is withdrawn from a measured volume of air inclosed in a tube. This is done by means of phosphorus.

To make the determination a graduated tube is filled with water and inverted in a vessel of water. A sample of the air to be analyzed is then introduced into the tube until it is nearly filled with

the gas, and the volume is carefully noted. A small piece of phosphorus is attached to a wire and brought within the tube as shown in Fig. 70. After a few hours the oxygen in the inclosed air will have combined with the phosphorus, the water rising to take its place. The phosphorus is removed, and the volume is again noted.

The contraction in the volume of the air is equal to the volume of oxygen absorbed.

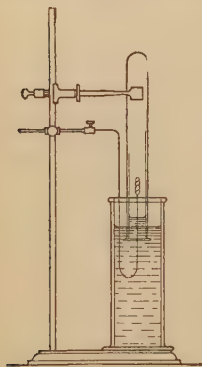


FIG. 70. The determination of the percentage of oxygen in air by means of phosphorus

2. Determination of nitrogen. If the gas left after the removal of oxygen from a portion of air is passed over heated magnesium, the nitrogen is withdrawn, leaving argon and the other rare elements. It may thus be shown that of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of air, approximately 78 are nitrogen and 0.94 argon. The other elements are present in such small quantities that they may be neglected.

3. Determination of water vapor and carbon dioxide. These constituents are determined by passing a known volume of air through two tubes, the first containing calcium chloride and the second sodium hydroxide (see arrangement of tubes, Fig. 64). The calcium chloride removes the moisture, while the sodium hydroxide removes the carbon dioxide. The increase in the weights of these two substances will give the weights of moisture and carbon dioxide respectively in the original volume of air.

Processes tending to change the composition of the air. These processes naturally fall into two classes: those which increase the carbon dioxide and those which diminish it.

1. Processes tending to increase the quantity of carbon dioxide. Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes and crevices in the earth's crust, but certain processes are constantly taking place which are

attended by evolution of this gas. Chief among these are the following: (a) *Respiration*. In this process some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon of the worn-out tissues. The products of oxidation are carried back to the lungs and exhaled largely in the form of carbon dioxide. (b) *Combustion*. All the ordinary fuels contain large percentages of carbon. On burning, this is oxidized to carbon dioxide. (c) *Decay of organic matter*. When organic matter decays in the air the carbon present is oxidized to carbon dioxide.

2. Processes tending to decrease the quantity of carbon dioxide.

There are two general processes which tend to diminish the quantity of carbon dioxide in the atmosphere:

(a) *The action of plants*. Plants have the power, when growing in sunlight, of absorbing carbon dioxide from the air, retaining the carbon and returning a portion of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

That plants evolve oxygen in the sunlight may be shown as follows: Some freshly gathered green leaves are placed under water in the jar *A* (Fig. 71) and covered with the funnel *B*, the stem of which extends into the graduated tube *C*, likewise filled with water. Bubbles of oxygen escape from the surface of the leaves and are caught in the measuring tube *C*.

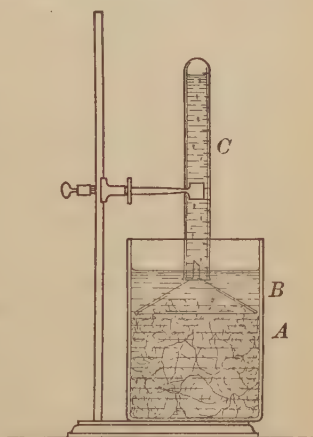


FIG. 71. The liberation of oxygen from plants exposed to sunlight

(b) *The weathering of rocks*. Large quantities of carbon dioxide are being constantly withdrawn from the atmosphere through its combination with various rock materials.

Composition of the air constant. Notwithstanding the changes constantly taking place which tend to alter the composition of the air, the results of a great many analyses of air collected in the open fields show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant. Indeed, so constant is the ratio of oxygen to nitrogen that the question has arisen whether air is not a definite chemical compound.

Air a mixture. That the oxygen and nitrogen in the air are not combined may be shown in a number of ways, among which are the following:

1. When air dissolves in water it has been found that the ratio of oxygen to nitrogen in the dissolved air is no longer 21 : 78, but more nearly 35 : 65. If air were a chemical compound, the ratio of oxygen to nitrogen would not be changed by solution in water.

2. A chemical compound in the form of a liquid has a definite boiling point at a given pressure. Water, for example, boils at 100° under standard pressure. The boiling point of liquid air, on the other hand, gradually rises as the liquid boils.

Why the air has a constant composition. If air is a mixture and changes are constantly taking place which tend to modify its composition, how, then, do we account for the constancy of composition which the analyses reveal? This is explained by several facts: (1) The changes which are caused by the processes of combustion, respiration, and decay, on the one hand, and the action of plants, on the other, tend to equalize each other. (2) The winds keep the air in constant motion and so prevent local changes. (3) The volume of air is so vast and the changes which occur are so small, compared with the total volume, that they cannot be readily detected. (4) Finally, it must be noted that only air collected in the open fields shows this constancy in composition. The air in a poorly ventilated room occupied by a number of people rapidly changes in composition.

Impure air and ventilation. The difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air are shown in the following table:

CONSTITUENT	INHALED AIR	EXHALED AIR
Oxygen	21.00 %	16.00 %
Carbon dioxide	0.04 %	4.38 %
Water vapor	variable	saturated

The injurious effects resulting from inadequate ventilation seem to be due neither to lack of oxygen nor to the excess of carbon dioxide; rather they are due to high temperature and to the presence of an abnormal amount of water vapor, both of which conditions are apt to prevail in crowded and poorly ventilated rooms.

One of the most important requirements for the well-being of the body is that its temperature be kept almost exactly constant (98.6°F.). Any marked deviation from this temperature is a serious matter. This temperature is kept up by the heat of combustion within the body, and if there were no opposing process, bodily temperature would exceed the safety point at times of great exertion or when the external temperature is high. Evaporation of water *absorbs* heat and so prevents undue rise in temperature. This evaporation takes place partly in the lungs and partly through the skin. When the air surrounding the body contains an abnormal percentage of water vapor this evaporation is greatly diminished and physical discomfort occurs.

Moreover, when the air is perfectly still that portion of the air in contact with the body tends to become saturated with moisture, and evaporation diminishes; hence the relief that comes from keeping the air in motion, as with an electric fan.

In general a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but it may be said to be about 30 cu. ft. per minute for each person present.

Liquid air. Air is now liquefied on a commercial scale by the apparatus already described (Fig. 32). Liquid air is essentially a mixture of liquid oxygen (boiling point, -183°) and

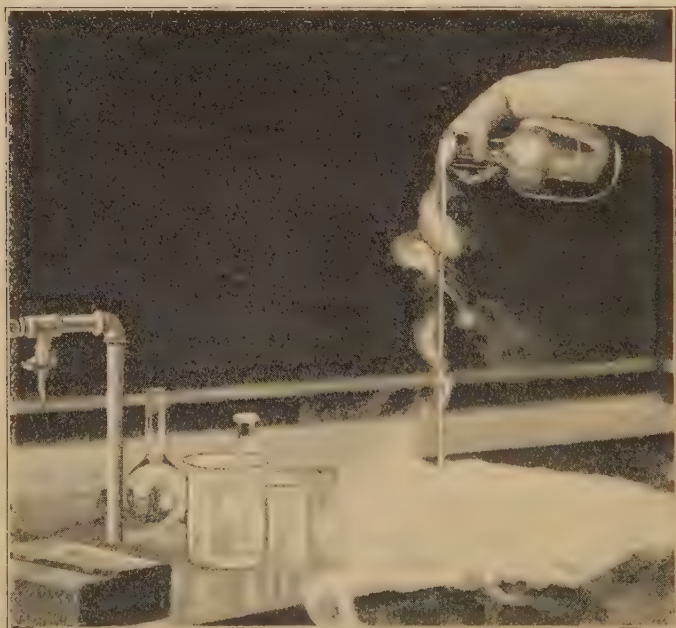


FIG. 72. Pouring liquid air from a thermos bottle

liquid nitrogen (boiling point, -195.7°) (Fig. 72). When air at ordinary temperatures heats this liquid, the gases pass off in the order of their boiling points, and in this way both oxygen and nitrogen are prepared for commercial purposes.

EXERCISES

1. When oxygen and nitrogen are mixed in the proportion in which they exist in the atmosphere, heat is neither evolved nor absorbed in the process. What important point does this suggest?
2. How does the air in manufacturing districts differ in composition from that in the open fields?

3. When ice is placed in a vessel containing liquid air the latter boils violently. Explain.

4. Does an electric fan lower the temperature (*a*) of a room? (*b*) of an individual in the room?

5. What is the meaning of the word *thermos*?

6. What is the cause of the cloud shown in Fig. 72?

7. Why must air be thoroughly dried before liquefying it?

8. What are some of the uses of liquid air?

9. Do you think it would be practicable to use liquid air for refrigerating purposes?

10. When liquid air boils which passes off first, oxygen or nitrogen?

11. Could animal life continue without the presence of carbon dioxide in the atmosphere?

12. Would combustion be more intense in liquid than in gaseous air?

13. In winter the processes (combustion and respiration) which tend to increase the volume of carbon dioxide in the air are very active, while the opposite process (the action of growing plants) takes place only to a small extent. Should you expect a sample of air collected in the winter to contain a larger percentage of carbon dioxide than one collected in the summer?

14. As a general average each person exhales about 460 liters of carbon dioxide daily. Calculate the weight of this volume of the gas.

15. Taking the volumes of the oxygen and nitrogen in 100 volumes of air as 21 and 78, respectively, calculate the percentages of these elements present in the air by weight.

16. Assuming that dry wood contains 40 per cent of carbon, all of which originally came from carbon dioxide in the air, what weight of carbon dioxide would have to be absorbed by a plant to make 500 g. of wood?

17. A tube containing calcium chloride was found to weigh 30.1293 g. A volume of air which weighed 15.2134 g. was passed through, after which the weight of the tube was found to be 30.3405 g. Find the percentage of moisture present in the air.

CHAPTER XIV

SOLUTIONS

Definitions. Everyone is familiar with the fact that when common salt is stirred in water, the salt disappears in the liquid. The chemist expresses this fact by saying that the salt *dissolves* in the water, and he calls the resulting product a *solution*. Just as the salt dissolves in water, so many other solids dissolve in water or other liquids forming solutions. In all such solutions the liquid is known as the *solvent*, and the dissolved solid is known as the *solute*. Thus in a solution of salt in water, the water is the solvent and the salt the solute.

It often happens that the solid does not really dissolve, but remains suspended in the liquid, rendering it cloudy. This is true of clay shaken with water. Upon standing quietly for some time, however, the matter in suspension gradually settles, while matter in true solution does not.

If we set aside in an uncovered dish any ordinary solution, such as a solution of common salt in water, the solvent gradually evaporates and the solid is recovered in its original state. The process may be hastened, of course, by heating the solution. In some cases solution is preceded by chemical action, and in such cases the original solid is not recovered upon evaporation. Thus, we say that sulfuric acid dissolves zinc. As a matter of fact, however, the acid changes the zinc into zinc sulfate, and it is not the zinc but the zinc sulfate which dissolves and which is recovered upon evaporation.

Saturated solutions. If we add a little salt to (say) 500 cc. of water in a beaker and stir it, it will readily dissolve. If we continue to add more of the salt, a little at a time, a

point will be reached finally at which the salt apparently no longer dissolves but settles to the bottom of the beaker, and we say that the solution is *saturated*. Experiments show that the salt *really continues to dissolve, but that the rate at which the solid dissolves is just balanced by the rate at which it separates again from the solution*. This condition may be described by saying that the solid and solution are *in equilibrium* with each other. *A solution is said to be saturated at a given temperature when it remains unchanged in concentration in contact with some of the solid*. The weight of the solid which will completely saturate a definite volume of the liquid at a given temperature is called the *solubility* of the substance at that temperature. It is usually expressed by stating the number of grams of solid that will dissolve in 100 cc. or in 1 liter of the liquid.

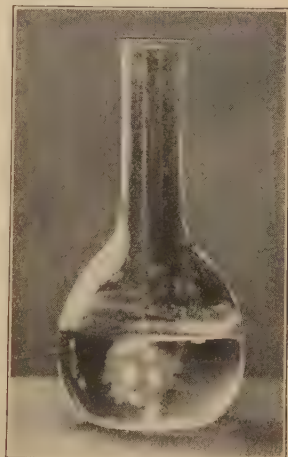


FIG. 73. The rapid growth of a crystal suspended in a supersaturated solution

Supersaturated solutions. Most solids are more soluble in hot than in cold liquids, and a liquid saturated at a high temperature usually deposits the excess of solute in the form of crystals as the temperature falls, maintaining saturation at all temperatures. Sometimes the crystals fail to form as the solution cools, especially if it is not disturbed in any way. The solution then contains more of the solute than is normally present when the solution is in equilibrium with the solid. Such a solution is said to be *supersaturated*. When a crystal of the solid is added to the supersaturated solution the excess of solute at once crystallizes out. This may be shown in a striking way by suspending a small crystal by a thread in a supersaturated solution (Fig. 73). The crystal grows rapidly in size, and fragments, breaking off, start crystallization at other points.

Classes of solutions. All gases mix freely with each other in all proportions, and such mixtures may be regarded as the solution of one gas in another. Gases, liquids, and solids dissolve in liquids, and one solid frequently dissolves in another. *The most familiar of these classes are solutions of gases or solids in liquids.*

Conditions affecting solubility. A number of different conditions influence the solubility of a substance in a liquid.

1. **Nature of the solute.** Each substance has its peculiar solubility just as it has its own odor, taste, or crystalline form. All substances may be regarded as being to some extent soluble in every liquid, but in many cases the solubility is so small that it cannot be measured. In other cases it is very great. Some solids dissolve in less than their own weight of water, and some gases, such as ammonia, dissolve to the extent of 1000 volumes in 1 volume of water.

2. **Nature of the solvent.** The nature of the solvent is no less important. Water and alcohol each has its own peculiar solvent power. Water is probably the most general solvent for all classes of materials, and alcohol is perhaps next to it. Ether, chloroform, and benzene are good solvents for organic substances such as fats, waxes, and oils, — a property that is utilized in removing grease spots from fabrics.

3. **Temperature.** The weight of a solid which a given liquid can dissolve varies with the temperature. Usually it increases rapidly as the temperature rises, so that the boiling liquid dissolves several times the weight which the cold liquid will dissolve. In some instances, as in the case of the solubility of common salt in water, the temperature has little influence, and a few solids are more soluble in cold water than in hot.

In the case of gases, on the other hand, *the lower the temperature of the liquid, the larger the volume of gas which it can dissolve.* While most gases can be expelled from a liquid by boiling the solution, some cannot.

Tables of solubilities. For convenience of reference the facts known about the solubilities of various substances have been collected into *tables of solubilities*, and these are constantly used by the chemist. Tables giving the solubilities of a few of the most familiar substances will be found in the Appendix.

4. **Pressure.** Change of pressure has little effect upon the solubility of a solid, but greatly influences that of a gas. *The weight of a gas which dissolves in a given case is proportional to the pressure exerted upon the gas* (Henry's law). If the pressure is doubled, the *weight* of the gas going into solution is doubled; if the pressure is diminished one half, then but half as much gas will dissolve. Under high pressure large quantities of a gas can be dissolved in a liquid, and when the pressure is removed the escape of the gas causes the liquid to foam, or *effervesce*, as in the familiar example of soda water.

Characteristic properties of solutions. A few general statements may be made in reference to some characteristic properties of solutions.

1. **Distribution of the solid in the liquid.** A solid, when dissolved, tends to distribute itself uniformly through the liquid, so that every part of the solution has the same concentration. The process goes on very slowly unless hastened by stirring or shaking the solution.

2. **Boiling point of solutions.** The boiling point of a liquid is raised by the presence of a substance dissolved in it. In general the extent to which the boiling point of a solvent is raised by a given substance is proportional not to the number of grams of the substance dissolved in a definite weight of the solvent, but to *the number of gram-molecular weights dissolved*. Thus the gram-molecular weight of glycerin ($\text{C}_3\text{H}_8\text{O}_3$) is 92, while that of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is 342; and 92 g. of glycerin dissolved in a definite weight of water will cause the same rise in the boiling point of the water as will 342 g. of sugar.

3. **Freezing point of solutions.** The freezing point of a liquid is lowered by the presence of a substance dissolved in it. The lowering of the freezing point obeys a law similar to the one which holds for the raising of the boiling point.

Electrolysis of solutions. Pure water does not appreciably conduct the electric current. If, however, certain compounds such as common salt or hydrochloric acid are dissolved in the water, the resulting solutions are found to be good conductors. Such compounds are called *electrolytes*. *When the current passes through a solution of an electrolyte some chemical change always takes place. This change is called electrolysis (p. 18).*

The general method used in the electrolysis of a solution is illustrated in Fig. 74. Two plates or rods, *A* and *B*, made of suitable material, are connected with the wires from a bat-

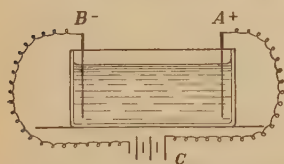


FIG. 74. Diagram showing the method of electrolysis of a solution

tery (or dynamo) *C* and dipped into the electrolyte, as shown in the figure. These plates or rods are called *electrodes*. The electrode *B* connected with the negative pole of the battery is the negative electrode, or *cathode*, while that connected with the positive pole *A* is the positive electrode, or *anode*.

The particular form of apparatus used varies in individual cases; thus in the electrolysis of water the electrodes are so arranged (Fig. 9) that the oxygen and hydrogen evolved may be collected.

In this way the electric current is utilized in bringing about chemical changes. It is being used more and more in the commercial preparation of many of the metals and their compounds. Thus the metal aluminium, used so largely in the construction of automobiles and culinary vessels, is obtained entirely by electrolysis. By the same process copper is purified and various objects are plated with gold and silver (electroplating).

EXERCISES

1. Give two examples of common solutions and name the solvent and solute in each case.
2. Distinguish between the following terms: (a) solution, (b) solvent, (c) solute, (d) saturated solution, (e) supersaturated solution.
3. Why does the water from some natural springs effervesce?
4. Explain the formation of the small bubbles that form in water that is being heated but has not yet reached the boiling point.
5. Why does not the water of the ocean freeze as easily as fresh water?
6. Suggest a method for raising the boiling point of water.
7. Do you see any reason for the common practice of adding salt to the water in which potatoes are to be boiled?
8. Why does a solid dissolve more rapidly when stirred?
9. Account for the fact that sugar often deposits from sirups, even when no evaporation has taken place.
10. Is it correct to define a saturated solution of any solid in a liquid as "one that contains all the solid the liquid will dissolve"?
11. (a) Why is alcohol added to the water used in the radiator of automobiles in cold weather? (b) Suggest some other substance that could be used in place of alcohol.
12. Wood alcohol (CH_3OH), grain alcohol ($\text{C}_2\text{H}_5\text{OH}$), and glycerin ($\text{C}_3\text{H}_8\text{O}_3$) are all soluble in water in all proportions. If you had 1 kg. of each, which would be the most effective for use to prevent the freezing of water in the radiator of an automobile?
13. Distinguish between the following terms: (a) electrolyte, (b) electrolysis, (c) electrode, (d) cathode, (e) anode.
14. Saturated solutions of each of the solids potassium nitrate, sodium chloride (common salt), and calcium hydroxide were prepared by heating the solids with 100 cc. of water at 100° . The resulting solutions were then cooled at 20° . What weight of solid separated in each case? (See Appendix for table of solubilities.)
15. (a) 10 g. of common salt was dissolved in water and the solution evaporated to dryness. What weight of solid was left? (b) 10 g. of zinc was dissolved in sulfuric acid and the solution evaporated to dryness. What weight of solid was left?

CHAPTER XV

CHLORINE; HYDROGEN CHLORIDE; HYDROCHLORIC ACID; ACIDS AND SALTS

Introductory. It is important that we should now learn something definite concerning the group of compounds known as *acids*. Before taking up the general subject we will first study a common and typical member of the group; namely, *hydrochloric acid*. This acid is a solution of a compound of the two elements hydrogen and chlorine. We have already studied hydrogen, and it is advisable for us to become acquainted with chlorine before proceeding with a study of hydrochloric acid.

Properties of chlorine. During the World War our papers and magazines had much to say concerning chlorine, for it was the first substance used by the Germans as a poison gas. Like most of the elements so far studied, chlorine is a gas, but, unlike them, it has a greenish-yellow color and a peculiar, suffocating odor. When inhaled, even in small quantities, it acts injuriously upon the throat and lungs, while in larger quantities it causes death; hence care must be taken in working with it not to breathe it. Chlorine is a heavy gas, being nearly 2.5 times as heavy as air. One volume of water under ordinary conditions dissolves 3 volumes of the gas.

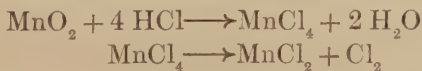
Occurrence. Chlorine does not occur free in nature, but its compounds are widely distributed. It is found in combination with the metals in the form of *chlorides*, those of sodium, magnesium, and potassium being the most abundant. All salt water contains these chlorides, particularly the one known as *sodium chloride* (NaCl), or *common salt*. Very large beds of chlorides (Fig. 81) are found in many parts of the world.

Historical. Chlorine was discovered by Scheele (p. 53) in 1774. It was thought to be a compound, however, until 1810, when the English chemist Sir Humphry Davy (Fig. 86) proved it to be an element and gave it the name which it now bears.

Preparation. Two general methods for preparing chlorine will be described: the laboratory method and the commercial method.

1. *Laboratory method.*

A common method for preparing chlorine in the laboratory consists in warming a mixture of hydrochloric acid and manganese dioxide (MnO_2). Manganese tetrachloride (MnCl_4) at first forms, but is unstable and breaks down into manganous chloride (MnCl_2) and chlorine (Cl_2), thus:



The manganese dioxide and the hydrochloric acid are brought together in a flask *A* (Fig. 75), and a gentle heat is applied. The chlorine set free escapes through the tube *B* and is collected in the cylinder *C* by displacement of air, the color showing when the cylinder is filled.

Instead of using hydrochloric acid in the preparation of chlorine, it serves just as well to use a mixture of sodium chloride and sulfuric acid, since these two react to form hydrochloric acid. In this case the complete reaction is expressed by the equation

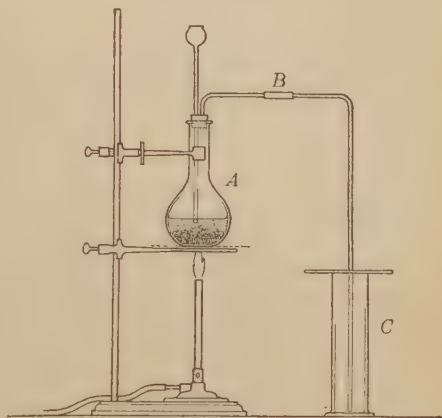
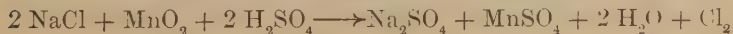


FIG. 75. Preparing chlorine by the action of hydrochloric acid on manganese dioxide

2. **Commercial method.** When an electric current is passed through an aqueous solution of sodium chloride (Fig. 74), chlorine is evolved at the anode and sodium is set free at the cathode. The sodium, however, as fast as liberated, reacts with the water present, forming hydrogen, which is evolved at the cathode, and sodium hydroxide, which remains dissolved in the water (p. 32). *The products of the reaction,*

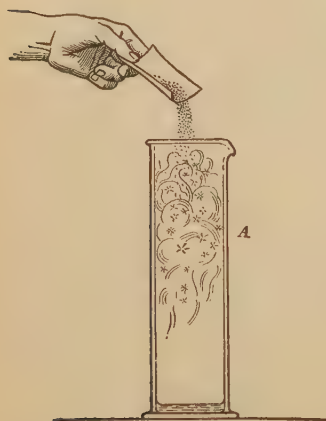


FIG. 76. The burning of powdered metals in chlorine gas

therefore, are chlorine, hydrogen, and sodium hydroxide. All the chlorine prepared for commercial purposes in the United States is obtained in this way. The method has advantages in that sodium chloride is cheap and that the sodium hydroxide formed in the process has many commercial uses. The chlorine so obtained is either used at the plant for bleaching, or is compressed in strong iron cylinders and shipped in this form, or is passed into slaked lime, forming the solid known as *chloride of lime* or

bleaching powder, which can be easily shipped and from which the chlorine can be recovered as needed.

The apparatus in which the electrolysis of the salt is carried out is known as a *cell* (Fig. 83), and there are several different kinds used, each being designated by the name of its inventor. The electrodes used are made of carbon.

Chemical conduct. At ordinary temperatures chlorine is far more active chemically than any of the elements we have so far considered ; indeed, it is one of the most active of all elements.

1. **Action on elements.** A great many elements combine directly with chlorine, especially when hot. A strip of hot copper

foil dropped into chlorine burns with incandescence. Antimony and arsenic in the form of a fine powder at once burst into flame when dropped into jars of chlorine (Fig. 76). The products formed in all cases where chlorine combines with another element are called *chlorides*.

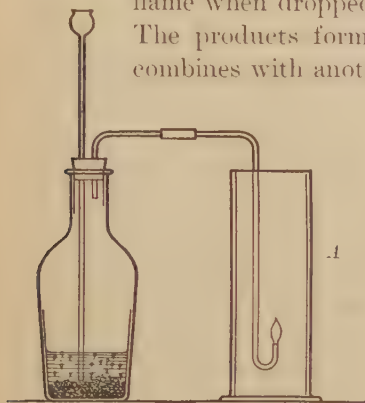


FIG. 77. The burning of a jet of hydrogen in an atmosphere of chlorine

2. Action on hydrogen. Chlorine has a particularly strong affinity for hydrogen, uniting with it to form hydrogen chloride. A jet of hydrogen burning in the air continues to burn when introduced into a jar of chlorine *A*. (Fig. 77), giving a somewhat luminous flame. A mixture of the two gases explodes violently when a spark is passed through it or when it is exposed to bright sunlight.

3. Action on substances containing hydrogen. Not only will chlorine combine directly with free hydrogen but it will often abstract the element from its compounds. Even water, which is a very stable compound, can be decomposed by chlorine, the oxygen being liberated. This may be shown in the following way:

Action of chlorine on water. A long tube of rather large diameter is filled with a concentrated solution of chlorine in water and inverted in a vessel of the same solution, as shown in Fig. 78, and the apparatus is placed in bright sunlight. Very soon bubbles of a gas will be observed to rise through the solution and collect in the tube, and an examination of this gas will show that it is oxygen.

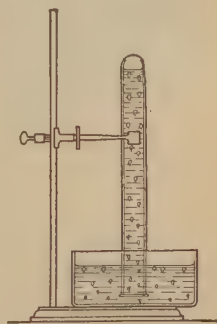
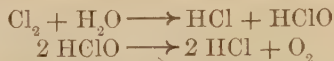


FIG. 78. Decomposition of water by chlorine in the sunlight

At first there is formed both hydrochloric acid and hypochlorous acid (HClO), but the latter is unstable and breaks down into HCl and O_2 .



4. *Action on color substances; bleaching action.* If strips of brightly colored cloth or some highly colored flowers are placed in *dry* chlorine, no marked change in color is noticed,



FIG. 79. Bleaching colored cloths by moist chlorine

as a rule. If, however, the cloth and flowers are first moistened, the color rapidly disappears, or, in other words, the objects are *bleached*. Evidently the moisture as well as the chlorine is concerned in the action. A study of the case shows that the chlorine sets the oxygen free from the water, as shown above, and the oxygen so liberated oxidizes the color substance (dye), converting it into a colorless compound. It is evident from this explanation that chlorine will bleach only those substances

which are changed into colorless compounds by oxidation. It has no action on such color substances as carbon and hence does not affect printer's ink made from carbon. It cannot be used for bleaching certain substances like silk and straw, since it injures the fabric.

Fig. 79 illustrates the bleaching action of chlorine. Strips from the same piece of cloth are suspended in three jars, of which the first contains air, the second *dry* chlorine, and the third *moist* chlorine. It will be noted that dry chlorine has almost no bleaching action, while the moist chlorine has partially removed the color.

5. *Action as a disinfectant.* Chlorine has also marked germicidal properties, and the free element, as well as compounds from which it is easily liberated, are used as disinfectants. It is also used to destroy the microorganisms in city water supplies (p. 65).

Bleaching. The process known as bleaching is an important one in connection with many industries. Thus the various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored; hence bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to air and sunlight, but the process was very slow. The same results are now obtained in a short time by the use of chlorine.

Uses. The normal production of chlorine in the United States amounts to nearly 500 tons daily. Most of this is used in bleaching fabrics and especially in the bleaching of wood pulp from which paper is made. It is also used in making *bleaching powder* and such compounds as chloroform (CHCl_3) and carbon tetrachloride (CCl_4). Increasing amounts are now compressed in strong steel cylinders called bombs (Fig. 80), and in this form shipped to points where it is needed for water purification and the preparation of various compounds.



FIG. 80. Chlorine stored in bombs for use in the purification of water

Chlorine in the World War. Nearly all the poison gases used in the World War were either free chlorine or compounds of chlorine. Poison gas was first used by the Germans on April 22, 1915, when a large quantity of chlorine, previously stored in cylinders hidden in the trenches, was allowed to escape. The gas, being heavy, clung to the ground and was carried forward by a favorable wind (Fig. 82). Later in the war the use of chlorine gave way largely to certain of its compounds which are more poisonous than the free element. Moreover, in place of trusting to the wind to carry the gas, the compounds were filled into shell and then fired into the ranks of the enemy. Because of the large demand for poison gas, large quantities of chlorine were required. To help meet the demand the United States built at Edgewood, Maryland, in 1917-1918, a chlorine plant with a daily capacity of one hundred tons, — the largest chlorine plant ever constructed (Fig. 83).

Nascent state. It will be noticed that when oxygen is set free from water by chlorine, it is at that instant able to do in a short period of time what ordinary oxygen gas cannot do, for it bleaches substances which would remain unchanged in air or pure oxygen for a long time. *It is generally true that the activity of an element is greatest at the instant of its liberation from its compounds.* To express this fact elements at the instant of liberation are said to be in the *nascent state*. When moist chlorine acts as a bleaching agent it is nascent oxygen which does the bleaching.

Hydrogen chloride (HCl): properties. Hydrogen chloride is a very important compound, since its solution in water constitutes ordinary *hydrochloric acid* (sometimes called *muriatic acid*), which has many commercial uses. It is a colorless gas and is 1.26 times as heavy as air. When inhaled, it has an irritating and suffocating effect. It is very soluble in water, 1 volume of water, under standard conditions, dissolving 506 volumes of hydrogen chloride. Hydrogen chloride, when exposed to the air, attracts moisture which condenses, forming little clouds or fumes.

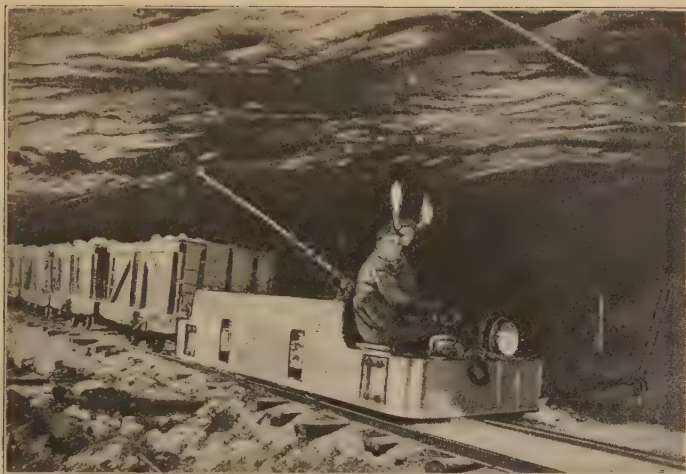


FIG. 81. Mining common salt (sodium chloride) for use in the manufacture of chlorine and hydrochloric acid

Mines of the Retsof Salt Company, near Rochester, New York

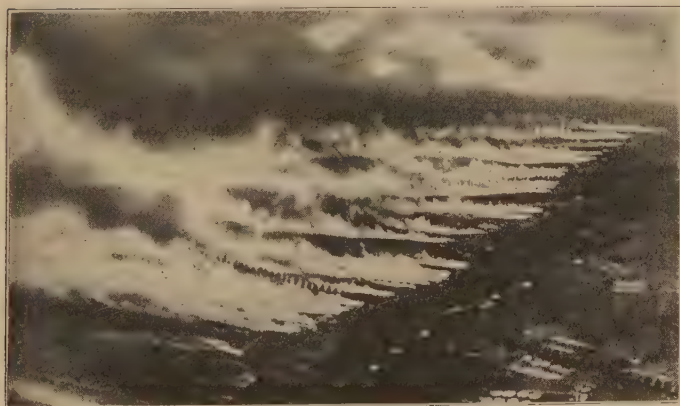


FIG. 82. A view of a chlorine-gas attack made by the French on the German trenches in Flanders during the World War

The chlorine was stored in cylinders placed in trenches, and when the wind was favorable the gas was released and was carried forward by the wind to the German trenches

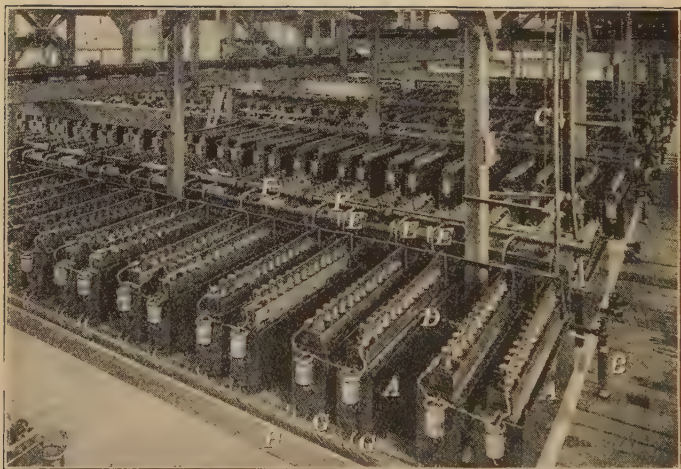


FIG. 83. View of one of the eight-cell rooms in the government chlorine plant built at Edgewood, Maryland, during the World War

This is the largest chlorine plant ever constructed, having a capacity of 100 tons of chlorine daily. The cells or compartments *A, A*, in which the sodium chloride is decomposed, are arranged side by side. A row of carbon rods *D* projects into each of the cells and constitutes the cathode, while the side of the cell constitutes the anode. A solution of salt enters the cells through the pipe *B*. The electric current enters through wires in *C* and decomposes the salt. The chlorine set free escapes from the cells through the pipes *E, E* into the larger pipe *F, F*, and is then conducted to the liquefying plant where it is liquefied and stored until desired for use. The sodium hydroxide formed flows from the cell through the pipes *G, G* into the trough *H* and is recovered by evaporating the water

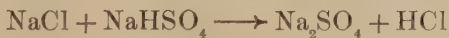
Preparation. The preparation of hydrogen chloride may be described under two general heads:

1. **Laboratory preparation.** While hydrogen chloride can be prepared by burning hydrogen in chlorine, it is much more conveniently obtained by treating common salt (sodium chloride) with sulfuric acid. The following equation shows the reaction :

$$2 \text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl}$$

The dry salt is placed in the flask *A* (Fig. 84), sulfuric acid is added, and the flask gently warmed. The hydrogen chloride is rapidly given off and can be collected by displacement of air. To prepare a solution of the gas the end of the delivery tube is fixed just above the level of some water in the cylinder *B*. The gas is very soluble and is absorbed as fast as it escapes from the tube.

2. **Commercial preparation.** Commercially, hydrogen chloride is prepared in connection with the manufacture of sodium sulfate, the reaction being the same as that just given. It is also prepared by heating sodium hydrogen sulfate (which is obtained in the manufacture of nitric acid) with sodium chloride :



In either case the hydrogen chloride liberated is passed into water, in which it dissolves, the solution forming the *hydrochloric acid* of commerce. When the materials are pure a colorless solution is obtained. The most concentrated solution has a density of about 1.2 and contains approximately 40 per cent

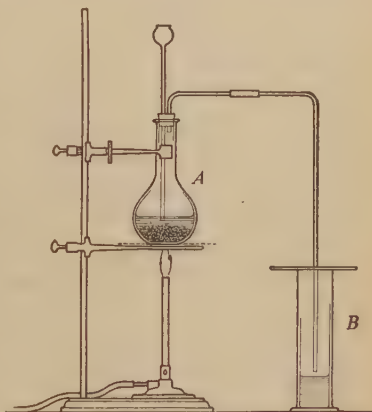


FIG. 84. The preparation of a solution of hydrogen chloride

by weight of hydrogen chloride. The commercial acid (often called *muriatic acid*) is usually colored yellow by impurities.

The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask *A* (Fig. 85) is filled with hydrogen chloride. This flask is connected, by means of a glass

tube, with a similar flask *B*, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask *A* is drawn out to a rather fine jet. By blowing into the tube *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from *B* into *A* until nearly all the hydrogen chloride is absorbed. It is evident that the connection must be air-tight.

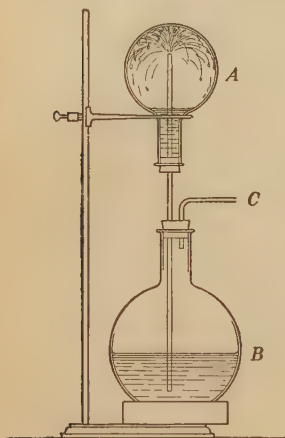


FIG. 85. Apparatus to show the extreme solubility of hydrogen chloride in water

Hydrochloric acid : properties and chemical conduct. While hydrogen chloride itself has but little chemical activity, its aqueous solu-

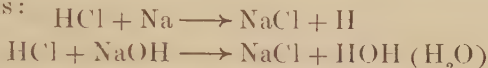
tion, namely, hydrochloric acid, has marked properties, the most important of which are as follows:

1. **Taste.** A dilute solution of the acid has a sour taste like that of vinegar.

2. **Action on colored compounds.** It acts upon many colored compounds and changes their color in some way — very often to a red. Thus, it changes the blue color of litmus (a coloring matter obtained from a plant) to red.

3. **Action upon metals and their hydroxides.** The hydroxides of the metals are compounds of a metal with hydrogen and oxygen, such as sodium hydroxide (NaOH). When hydrochloric acid is brought in contact with certain metals or with the

hydroxide of the metals, the hydrogen of the acid is replaced by the metal, thus:



Acids. Hydrochloric acid is one of a large number of important solutions known collectively as the *acids*. Thus, in addition to hydrochloric acid we have nitric acid, which is a solution of the liquid known as hydrogen nitrate (HNO_3), and sulfuric acid, which is a solution of an oily liquid called hydrogen sulfate (H_2SO_4). For most purposes it is not necessary to distinguish in name between these compounds and their solutions in water, and *both are frequently called acids*.

The characteristic properties of acids are in the main those given above for hydrochloric acid. *We may there-*



FIG. 85 A. The three most common acids used in the laboratory

fore define an acid as a compound of hydrogen whose aqueous solution (1) has a sour taste, (2) changes blue litmus to red, and (3) acts upon metals and their hydroxides, forming compounds in which the hydrogen of the acid is replaced by the metal.

Just as the individuals composing a group of people have certain characteristics in common and yet may differ widely in certain traits, so the acids, although possessing many common properties, may differ in other properties. Thus, some are more easily decomposed than others; some are very poisonous, while others are not.

Salts. We have seen in the discussion of acids that the hydrogen of the acid may be displaced readily by a metal. The resulting compound is known as a *salt*. *A salt may therefore be defined as a compound derived from an acid by replacing the hydrogen of the acid by a metal.*

Since salts are derived from acids we speak of the salts of the acids. Thus, sodium chloride (NaCl) is a salt of hydrochloric acid (HCl), while copper sulfate (CuSO_4) is a salt of sulfuric acid (H_2SO_4). We might expect each acid to form as many salts as there are metals. This is not true, however, since some of the salts are unstable and have never been prepared. Nevertheless the number of salts is very large.

Radicals and their valence. If we compare the formulas H_2SO_4 , Na_2SO_4 , and CuSO_4 , it will be noticed that they all contain the group of atoms SO_4 . Similarly, the compounds represented by the formulas HOH , NaOH , and KOH all contain the group of atoms OH , known as the *hydroxyl* group. *Groups of atoms which act together as a unit in chemical action are called radicals.* Radicals do not exist in a free state but only in combination with other atoms or radicals. Oftentimes a molecule may contain more than one hydroxyl or other radical. Thus, calcium hydroxide contains 1 atom of calcium and 2 hydroxyl groups in each molecule. In such cases it is customary to write the formula $\text{Ca}(\text{OH})_2$ rather than CaO_2H_2 , although either is correct. Similarly, we write $\text{Al}_2(\text{SO}_4)_3$ rather than $\text{Al}_2\text{S}_3\text{O}_{12}$, and $\text{Ca}_3(\text{PO}_4)_2$ rather than $\text{Ca}_3\text{P}_2\text{O}_8$.

The valence of a radical can be determined by noting the number of atoms of hydrogen (or some other univalent element) with which it combines. The radical SO_4 is bivalent, for it combines with two hydrogen atoms as represented in the formula H_2SO_4 . The radical OH , on the other hand, is univalent, for it combines with one atom of hydrogen to form water (HOH or H_2O).

Formulas of salts. Knowing the valence of a metal and the formula of any acid it is easy to deduce the formula of the salt which the metal may naturally be expected to form with the acid. Thus, suppose we wish to write the formulas of the salt which the element calcium forms with the acids HCl ,

H_2SO_4 , and H_3PO_4 respectively. First write the symbol of the element in place of the hydrogen of the acid:



Now write over the symbols of calcium, chlorine, and each of the radicals SO_4 and PO_4 the valence of each element or radical:



Finally, take such numbers of the two constituents of each salt as will add up an equal number of valences. This gives the following as the correct formulas:



Naming of acids. The method of naming acids depends upon whether the acid consists of two elements or of three.

1. **Binary acids.** Acids containing only one element in addition to hydrogen are called *binary acids*. They are given names consisting of the prefix *hydro-*, the name of the second element present, and the termination *-ic*. Examples: hydrochloric acid (HCl) and hydrosulfuric acid (H_2S).

2. **Ternary acids.** In addition to the two elements present in binary acids, most acids also contain oxygen. These acids therefore consist of three elements and are called *ternary acids*. It is the element other than hydrogen and oxygen which gives its name to the acid. It usually happens that the same three elements can unite in different proportions to make several different acids. The most familiar one of these is given a name ending in the suffix *-ic*, while the one with less oxygen is given a similar name, but ends in the suffix *-ous*. Examples: nitric acid (HNO_3) and nitrous acid (HNO_2).

In cases where more than two acids are known, use is made of prefixes in addition to the suffixes *-ic* or *-ous*. Thus the prefix *per* signifies an acid still richer in oxygen; the prefix *hypo* signifies one with less oxygen. Thus HNO , if it existed, would be called hyponitrous acid, while HNO_4 would be called pernitric acid.

Naming of salts. A salt derived from a binary acid is given a name consisting of the names of the two elements composing it, with the termination *-ide*. Example: sodium chloride (NaCl). All other binary compounds are named in the same way.

A salt of a ternary acid is named in accordance with the acid from which it is derived. A ternary acid with the termination *-ic* gives a salt with the name ending in *-ate*, while an acid with the termination *-ous* gives a salt with the name ending in *-ite*. The following table, giving a number of examples, will make the application of these principles clear:

ACID	FORMULA	SALT	FORMULA
Hydrochloric	HCl	Sodium chloride	NaCl
Chlorous	HClO_2	Sodium chlorite	NaClO_2
Chloric	HClO_3	Sodium chlorate	NaClO_3

Chlorides. Since each acid forms a number of salts it is convenient after describing any acid to note the general properties of its salts. Having now studied hydrochloric acid we may add that the salts of this acid, namely, *the chlorides*, are with few exceptions solid compounds and are all soluble in water except silver chloride and mercurous chloride. Lead chloride is soluble in hot water, but not in cold.

EXERCISES

1. What is the significance of the terms *chlorine* and *nascent*? (Consult dictionary.)
2. Why are laboratory methods of preparation so often different from commercial methods?
3. What factors enter into the cost of any substance such as chlorine and hydrochloric acid?
4. If you were going to build a plant for the commercial preparation of chlorine, what factors should you take into consideration in selecting a location for the plant?

5. Mention three discoveries made by Scheele.
6. Why is printer's ink not bleached by chlorine?
7. Chlorine has only a comparatively slight color, and this would not affect the photographic plate. How, then, account for the cloud shown in Fig. 82?
8. Distinguish (a) between atoms and radicals; (b) between acids and salts.
9. Name three foods or drinks that taste sour. How could you prove that acids are present in them? *apple, lemon*
10. Name the following compounds and designate to which class (acids or salts) each belongs: HBr , HCl , H_2S , KBr , MgBr_2 , CuS .
11. How can you determine the valence (a) of atoms? (b) of radicals?
12. The most common of the ternary acids of sulfur is H_2SO_4 . Name the following compounds and designate to which class (acids or salts) each belongs: H_2SO_4 , H_2SO_3 , H_2SO_2 , Na_2SO_4 , ZnSO_4 , Ag_2SO_3 , Na_2SO_2 .
13. The most common of the ternary acids of phosphorus is H_3PO_4 . (a) What is its name? (b) What is the valence of the radical PO_4 ? (c) Derive the formula for the salts that you would expect the above acid to form with each of the metals sodium, zinc, and aluminium.
14. Suppose you wished to prepare 5 liters of chlorine in the laboratory. What materials and what weight of each would you require?
15. Calculate the percentage of chlorine in sodium chloride.
16. A plant for the production of chlorine has an output of 18 tons of chlorine daily. What weight of sodium chloride would be required daily?
17. (a) What is the weight of 1 liter of concentrated hydrochloric acid? (Density = 1.2.) (b) What weight of hydrogen chloride does it contain (pp. 143, 144)? (c) What weight of sodium chloride would be required to prepare this weight of hydrogen chloride?

CHAPTER XVI

SODIUM; SODIUM HYDROXIDE; BASES

Metals and nonmetals. The chemist finds it convenient to divide the elements into two general groups known as the *metals* and the *nonmetals*. It is the chemical conduct of an

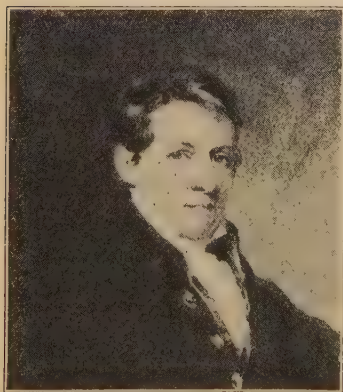


FIG. 86. Sir Humphry Davy
(1778-1829)

A distinguished English scientist who proved that chlorine is an element and first isolated the elements sodium and potassium

element that determines to which of these two groups it belongs. This distinction will be described more fully in a later chapter. For the present it is only necessary for us to remember that all the metals are solids (except mercury, which is a liquid), that as a rule they are good conductors of heat and electricity, and (with the exception of gold and copper) that they have a silvery luster. Most of the metals have a high density; a few, such as aluminium and magnesium, however, are comparatively light; while three (namely, lithium, sodium, and

potassium) are so light that they will float on water.

The elements so far studied are all nonmetals. It is advisable now to study some one metal, and the one known as *sodium* best serves our purpose.

General discussion. Sodium was first prepared in 1807 by Davy (Fig. 86), who isolated it by passing an electric current

through melted sodium hydroxide. It is a silver-white metal, a little lighter than water, and so soft that it can be molded easily by the fingers or pressed into wire. It melts at 97.5° . It is very active chemically, combining with most of the non-metallic elements, such as oxygen and chlorine. It displaces hydrogen from acids (p. 145) as well as from water (p. 31). Because of its affinity for oxygen, it tarnishes immediately on exposure to air; hence it is often kept immersed in kerosene, since it has no action upon this liquid.

Occurrence of sodium. Sodium does not occur in nature in a free state. The most familiar compound of the element found in nature is *sodium chloride*. This is a constituent of all sea waters and mineral waters and forms large solid deposits in various parts of the world (Fig. 81). The element also occurs as a constituent of many rocks, and its compounds are therefore present in the soil formed by their disintegration. Other compounds of sodium often found in nature are *sodium nitrate* (known commercially as *Chile saltpeter*), *sodium carbonate*, and *sodium borate*, or *borax*.

Preparation. Sodium is prepared by the same method which led to its discovery; namely, by passing an electric current through melted sodium hydroxide. Water must be excluded; otherwise the sodium, as fast as it is liberated, will react with the water to form sodium hydroxide.

Technical preparation. The sodium hydroxide is melted in a cylindrical iron vessel *A* (Fig. 87) through the bottom of which rises the cathode *B*. The anodes *C*, several in number, are suspended

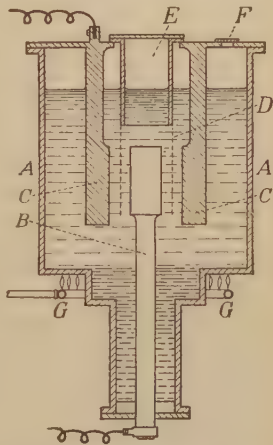


FIG. 87. A Castner cell for the electrolytic production of metallic sodium

around the cathode from above. A cylindrical vessel *E* floats in the fused alkali, directly over the cathode, and under this cap the sodium and hydrogen liberated at the cathode collect. The hydrogen escapes by lifting the cover, and the sodium, protected from the air by the hydrogen, is from time to time skimmed or drained off. Oxygen is set free upon the anode and escapes into the air through the opening *F* without coming into contact with the sodium or the hydrogen.

Uses. Sodium is used in preparing certain of its compounds. It is also used in making the well-known dye indigo.

Compounds of sodium. Sodium forms many useful compounds. One of these, *sodium hydroxide*, is a typical member of that important class of compounds known as *bases*, and it is desirable for us to study its properties at this time; the discussion of the other compounds of sodium may well be deferred to a later chapter.



FIG. 88. The form of sodium hydroxide used in the laboratory

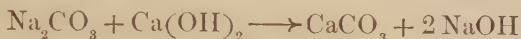
Sodium hydroxide (caustic soda) (NaOH).

Sodium hydroxide is a brittle, white crystalline substance which rapidly absorbs water and carbon dioxide from the air. For laboratory purposes it is ordinarily sold in the form of sticks resembling sticks of white candy (Fig. 88). It is very soluble in water, and it is the solution that is commonly used. As the name *caustic soda* indicates, it is a very corrosive substance, having a disintegrating action on most animal and vegetable tissues. It is used

in a great many chemical industries, its chief uses being in the manufacture of soap and paper and in refining petroleum. As a household article it is sold under the name of *lye*.

Preparation. Sodium hydroxide is prepared commercially by two different processes, as follows:

1. In the older process sodium carbonate is treated in solution with calcium hydroxide (slaked lime). Calcium carbonate is precipitated according to the equation



The dilute solution of sodium hydroxide, filtered from the insoluble calcium carbonate, is evaporated to dryness; the solid is then melted and poured into molds to solidify. Most of the sodium hydroxide is made by this method.

2. The newer method consists in the electrolysis of a solution of sodium chloride as explained under chlorine (p. 138). Every chlorine plant is, therefore, a plant for producing sodium hydroxide.

Chemical conduct. Sodium hydroxide has certain properties in common with the hydroxides of other metals. These common properties are as follows:

1. **Action on litmus.** Its action on litmus (as well as on other colored substances) is just the opposite of that of acids; that is, it turns red litmus to a blue color.

2. **Action on acids.** It reacts with acids to form salts and water (p. 145),



Bases; alkalies. Sodium hydroxide is one of a group of compounds, each member of which is composed of a metal combined with one or more OH radicals. Thus we have sodium hydroxide (NaOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$), and copper hydroxide ($\text{Cu}(\text{OH})_2$). These compounds are known collectively as *bases*. Like the acids, their basic properties are developed only in the presence of water, but as a rule no distinction in name is made between the compound and its solution. *Therefore a base may be defined as a compound of a metal and one or more OH groups. In the presence of water (1) it changes red litmus to a blue color and (2) it reacts with acids to form salts and water.*

Those hydroxides which have the most highly developed basic properties are often called *alkalies*. The common alkalies are sodium hydroxide, potassium hydroxide, and calcium hydroxide.

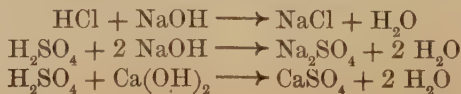
Neutralization. We have seen that when an acid and a base are brought together a reaction takes place which consists in the interchange of the hydrogen of the acid and the metal of the base, forming a salt and water, thus :



The interaction of an acid and a base to form a salt and water is known as neutralization, and the acid and the base are said to neutralize each other. It is evident from the above equation that both the acid and the base disappear as such in the reaction, and in their places we have a salt and water. By evaporation of the water the salt may usually be obtained in pure form. Neutralization, therefore, serves as a general method for the preparation of salts.

Indicators. We have seen that acids turn blue litmus to a red color, while bases reverse the change, turning red back to blue. We may employ litmus, therefore, to determine whether a given solution is acid or basic. It may also be used to determine whether or not a solution is *neutral* (that is, neither acid nor basic), for such solutions will have no effect on either blue or red litmus. In addition to litmus, certain other colored compounds may be used for determining whether solutions are acid, basic, or neutral; and all these are known collectively as *indicators*.

Balancing equations of neutralization. In neutralization the hydrogen of the acid combines with the hydroxyl radical (OH) of the base to form water; hence in balancing equations representing neutralization we must take the acid and the base in such proportions that the number of hydrogen atoms of the acid will be the same as the number of hydroxyl radicals of the base, thus :



EXERCISES

1. What is the word from which the symbol of sodium is derived? (Consult dictionary.) \

2. (a) Is sodium an abundant element? (b) What weight of it is in your body?

3. The ordinary conception of a metal is a substance that is heavy and hard. Is this view correct from a chemical standpoint?

4. Are there any metals that are liquids at ordinary temperatures?

5. In the commercial preparation of what element do we also obtain sodium hydroxide?

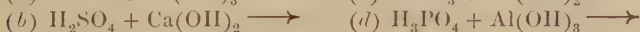
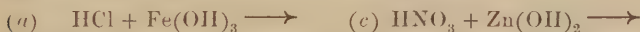
6. Distinguish between (a) acids, (b) salts, (c) bases, and (d) alkalies.

7. If you knew that a liquid contained either hydrochloric acid or sodium hydroxide, how could you easily decide which is present?

8. Does sugar ($C_{12}H_{22}O_{11}$) neutralize an acid in foods or simply mask it?

9. If your clothing becomes spotted with acids, how would you try to remove these spots?

10. Complete and balance the following equations:



11. Some soils are acid in character and will not grow certain crops, such as clover and alfalfa. (a) How could you tell if a given soil is acid? (b) If acid, suggest a method for correcting the acidity.

12. What weight of sodium is present in 100 g. of sodium hydroxide?

13. For every ton of chlorine made commercially, how many pounds of sodium hydroxide are formed?

14. What weight of hydrogen chloride is necessary to neutralize 100 g. of sodium hydroxide?

15. What weight of sulfuric acid (hydrogen sulfate) will be neutralized by 40 g. of sodium hydroxide?

CHAPTER XVII

IONIZATION

Introductory. Pure water does not appreciably conduct the electric current, or, as we say, it is a *nonconductor*. If certain compounds, such as sugar, are dissolved in the water, the solutions are also nonconductors. If, however, certain other compounds, such as sodium chloride, hydrogen chloride, or sodium hydroxide, are dissolved in the water, the resulting solution is found to be a conductor. *A compound whose solution conducts the electric current is called an electrolyte.* It has been found

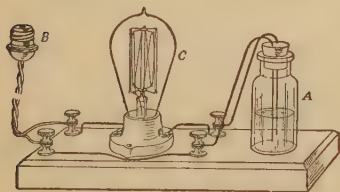


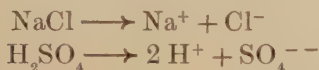
FIG. 89. A convenient form of apparatus for determining whether or not a substance is a conductor of electricity

by experiment that *all acids, bases, and salts are electrolytes.* We have already seen that the electric current in passing through such a solution causes certain chemical changes (electrolysis, p. 134).

Fig. 89 illustrates a very convenient apparatus for determining whether a solution is a good conductor. The solution is placed in the bottle *A* and the electrodes are dipped into it. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.

Theory of ionization. In order to explain the facts just stated, as well as many others, the Swedish chemist Arrhenius (Fig. 90), in 1887, proposed a theory known as the *theory of ionization*. Its main points are as follows:

It is supposed that the molecules of all electrolytes when dissolved in water tend to fall apart into two kinds of atoms, or groups of atoms, known as *ions*, and that it is these ions which carry the electric current through the solution. Moreover, each of the two kinds of ions formed from any molecule are highly charged with electricity; these charges, however, are equal and opposite in character, so that the solution, as a whole, is electrically neutral. The chemist expresses these facts as follows, using NaCl and H_2SO_4 as examples:



It is not to be supposed that in every solution *all* the molecules are ionized. The percentage of molecules ionized depends (1) *upon the compound*, (2) *upon the solvent* (water is the best ionizing solvent), and (3) *upon the amount of water*

present, the greater the amount of water present the greater the percentage of molecules ionized. In all such solutions the molecules are in equilibrium with the ions, some molecules falling apart into ions, while other ions are recombining to form molecules as expressed in the equation



The double arrows are used to indicate the fact that the action is going on in both directions, the result being a state of equilibrium.



FIG. 90. Svante August Arrhenius
(1859-)

A Swedish chemist who suggested
the theory of ionization

Since solutions of salt contain the ions Na^+ and Cl^- , the question might arise as to why such a solution shows no evidence of sodium and chlorine. The reason is that sodium and chlorine are greatly modified in properties by the high charge of electricity which they carry as ions. Thus the sodium ion does not decompose water; if, however, we could discharge the ion, it would then become an atom of sodium and would at once decompose the water. We shall see later how this can be done.

To be of value the above theory must give a satisfactory explanation of the properties of solutions. We shall now see if the theory meets this test.

The theory of ionization and electrolysis. We have learned (p. 138) that when an electric current is passed through a solution of sodium chloride there are formed hydrogen, chlorine, and sodium hydroxide. The

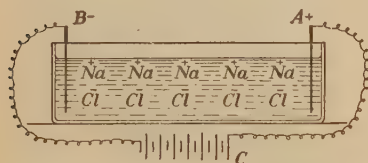


FIG. 91. A diagram illustrating the theory of the electrolysis of sodium chloride (NaCl)

theory of ionization accounts for the formation of these products from the salt in the following way: The solution of salt contains the ions Na^+ and Cl^- (Fig. 91). Now suppose that we place in the solution the electrodes A and

B , connected with the battery C , so that A forms the anode and B the cathode. The anode A being positively charged attracts the negatively charged chlorine (unlike electric charges attract each other). The chlorine ions, on reaching the anode, give up their charge and then combine to form molecules and are evolved as free chlorine. The sodium ions, on the other hand, are attracted to the negatively charged cathode B . On coming in contact with the cathode they give up their charge and, being now ordinary sodium atoms, at once decompose the water present, forming hydrogen and sodium hydroxide (p. 31).

It is to be carefully noted that the current does not bring about the decomposition of the electrolyte into ions, but can pass through the solution only when ions are already present.

Acids, bases, neutralization, and salts from the standpoint of the theory of ionization. Acids, bases, and salts are all electrolytes, hence they are ionized in solutions.

1. **Acids.** All acids ionize in solution, forming positively charged hydrogen ions, while the remainder of the molecule forms the negatively charged ion. The hydrogen ion is common to all acids, while the other ion varies with the acid.



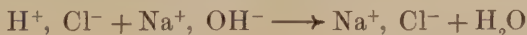
Hence the common properties of acids, such as their taste and their action on litmus and metals, must be due to the hydrogen ions. From the standpoint of the theory of ionization *an acid may be defined as a compound which produces hydrogen ions when dissolved in water.*

2. **Bases.** All bases ionize, forming a metal ion and a hydroxyl ion, thus:



The metal ion varies according to the base, but the hydroxyl ion is common to all; hence the common properties of bases must be due to the hydroxyl ions. *A base may therefore be defined as a compound which produces hydroxyl ions when dissolved in water.*

3. **Neutralization and salts.** Experiments show that hydrogen ions and hydroxyl ions, when brought together, at once unite to form water, a compound which is at most but slightly ionized. If, then, an acid and a base are brought together, the hydrogen ions of the acid and the hydroxyl ions of the base unite, thus:



If the water is evaporated, the Na^+ of the base and the Cl^- of the acid gradually unite to form the salt NaCl . From

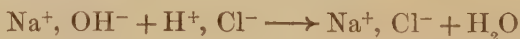
the standpoint of the ionization theory, therefore, the terms *neutralization* and *salt* may be defined as follows:

Neutralization consists in the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water.

A salt is a compound formed by the union of the negatively charged ion of an acid with the positively charged ion of a base.

Strength of acids and bases. Since acid and basic properties are due to hydrogen ions and hydroxyl ions, the acid or base which will produce the greatest percentage of these ions at a given concentration must be regarded as the strongest representative of its class. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half of the molecules are dissociated into ions, and this is also approximately the extent to which most salts are ionized at this same concentration.

Methods of expressing reactions between compounds in solution. Chemical equations representing reactions between substances in solution may represent the details of the reaction, or they may simply indicate the final products formed. Thus, if we wish to call attention to the details of the reaction between sodium hydroxide and hydrochloric acid in solution, representing the ions which take part in the reaction, we write the equation as follows:



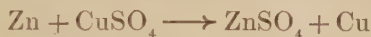
If, on the other hand, we wish simply to represent substances taking part in the reaction and the final products formed, we write the equation thus:



Displacement (or electrochemical) series. Upon bringing a piece of zinc into an acid, zinc passes into solution and hydrogen is evolved:



In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate CuSO_4 , zinc passes into solution, and a corresponding quantity of copper is precipitated:



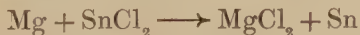
On the other hand, copper has no effect upon a solution of zinc sulfate.

It has been found to be possible to arrange hydrogen and the metals in a table in such a way that any element in the list will displace any one *below* it from its salts and will in turn be displaced from its salts by any one *above* it. This list is called the *displacement series* or the *electrochemical series*.

DISPLACEMENT (ELECTROCHEMICAL) SERIES

1. Potassium	7. Manganese	13. Tin	19. Antimony
2. Sodium	8. Zinc	14. Lead	20. Mercury
3. Lithium	9. Chromium	15. Hydrogen	21. Silver
4. Calcium	10. Iron	16. Copper	22. Platinum
5. Magnesium	11. Cobalt	17. Arsenic	23. Gold
6. Aluminium	12. Nickel	18. Bismuth	

This table enables us to foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts:



We should not, however, expect iron to displace aluminium.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from acids, while those below it will not. In the latter case, if any action takes place it is preceded by oxidation.

It will be recalled that sodium liberates hydrogen from water as well as from acids. All the metals above hydrogen do this, though in many cases the action is very slow.

EXERCISES

1. State reasons why chemists believe that the molecules of some compounds separate into parts when dissolved in water while others do not.
2. Distinguish clearly between atoms and ions.
3. In accordance with the theory of ionization a solution of sodium chloride in water contains sodium ions. Why does not the sodium decompose the water?
4. What is the difference in composition between a concentrated solution of sodium chloride and a dilute one?
5. How do we account for the fact that a substance develops acid properties only when dissolved in water or some similar liquid?
6. A solution of hydrogen chloride in the liquid known as benzene does not conduct the electric current. Should you expect this solution to have acid properties?
7. From the standpoint of the ionization theory what is the change that takes place in neutralization?
8. Tin dissolves in hydrochloric acid. Will hydrogen be evolved in the process (see displacement series)?
9. What metals cannot be used for preparing hydrogen?
10. What metals displace hydrogen from water? What ones have we actually used for this purpose?
11. Should you expect any relation to exist between the position of an element in the displacement series and the probability of its occurrence in a free state in nature?
12. A strip of iron is placed in a solution of copper sulfate (CuSO_4). Should you expect any reaction to take place?
13. Will either copper or silver react with water (see displacement series)?
14. Suppose you were to electrolyze a solution of a salt of either copper or silver, what would become of the metals?
15. From the standpoint of the ionization theory write the equation for the reaction between nitric acid and sodium hydroxide.

CHAPTER XVIII

COMPOUNDS OF NITROGEN

Occurrence. The large quantity of nitrogen occurring in the atmosphere (p. 122) is practically all in the free state. In the materials composing the earth's crust, on the other hand, there occur in certain localities considerable deposits of nitrogen compounds, especially of sodium nitrate (NaNO_3). Small quantities of nitrogenous compounds also occur in all productive soils. From these soils the nitrogen is taken up by plants and built into complex compounds known as *protein* matter. Animals feeding on these plants assimilate the nitrogenous matter, which becomes an essential part of the animal tissue.

While a great many compounds of nitrogen are known, it is desirable at this time to study only a few of the simpler ones.

AMMONIA (NH_3)

Several compounds consisting exclusively of nitrogen and hydrogen are known, but only one, ammonia, need be considered here. A solution of this compound in water (ammonia water) is a familiar substance, since it is used in our homes both as a medicine and as a cleansing agent.

Properties. Under ordinary conditions ammonia is a gas which is little more than half as heavy as air. It is colorless and has a strong, suffocating odor often noticed about decaying organic matter. It is extremely soluble in water, 1 liter of water at 0° and 760 mm. pressure dissolving 1298 liters of the gas, and at 20° and the same pressure 710 liters. In dissolving such large volumes of the gas the water expands considerably,

so that the density of the solution is less than that of water, the most concentrated commercial solutions having a density of 0.88. Ammonia is easily condensed into a colorless liquid, and can now be purchased in this form.

Preparation of ammonia. Ammonia can be prepared in the laboratory by a simple method, but the industrial methods require elaborate apparatus.

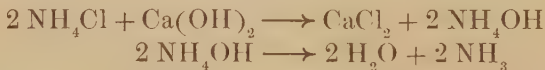
1. **Laboratory method.** In the laboratory ammonia is prepared from ammonium chloride (NH_4Cl), a white solid obtained in the manufacture of coal gas. In this compound the group NH_4 acts as a univalent radical and is known as *ammonium*. When ammonium chloride is warmed with sodium hydroxide *the ammonium radical and sodium change places*, the reaction being expressed in the following equation:



The ammonium hydroxide (NH_4OH) so formed is unstable and breaks down into water and ammonia:



Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is frequently used in place of the more expensive sodium hydroxide, the equations being



The ammonium chloride and calcium hydroxide are mixed together and placed in a flask *A*, arranged as shown in Fig. 92. The mixture is gently warmed, when ammonia is evolved as a gas and, being much lighter than air, is collected in *B* by displacement of air, as shown in the diagram.

2. **Preparation from coal.** Ordinary soft coal contains small percentages of nitrogen and hydrogen, along with the carbon, and when the coal is heated in the absence of air (see coal gas) a part of this nitrogen and hydrogen is converted into ammonia.

The gas is purified, and either dissolved in pure, cold water, forming *aqua ammonia*, or absorbed by acids with which it unites to form solid compounds. Nearly all the ammonia used in the United States comes from this source. A limited amount is prepared from cyanamide, as will be explained later.

3. **The Haber process.** When a mixture of nitrogen and hydrogen subjected to a pressure of 200 atmospheres is heated to about 500° in contact with a suitable catalyzer, about 8 per cent of the nitrogen present combines with hydrogen. The resulting ammonia is dissolved in water as fast as formed, and the remaining gases are again conducted over the catalyzer. The process thus becomes continuous, more nitrogen and hydrogen being introduced as needed. The nitrogen used is obtained from the air, and the hydrogen is obtained from water. During the war the Germans prepared large quantities of ammonia by this process. Moreover, it is probable that this method will come into general use as coal becomes scarcer. The method was devised by a German chemist named Haber; hence the name *Haber process*.

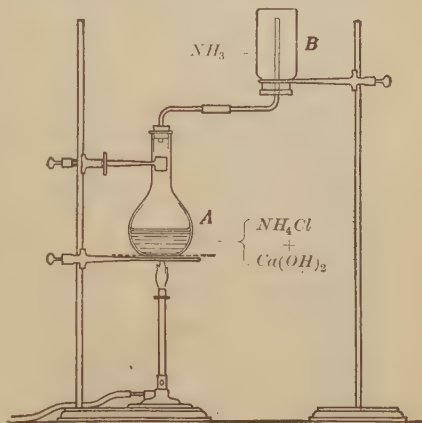


FIG. 92. The preparation and collection of ammonia in the laboratory

large quantities of ammonia by this process. Moreover, it is probable that this method will come into general use as coal becomes scarcer. The method was devised by a German chemist named Haber; hence the name *Haber process*.

Chemical conduct. Ammonia will not support combustion nor will it burn under ordinary conditions. In an atmosphere of oxygen it burns with a feeble, yellowish flame. When quite dry it is not a very active substance, but when moist it combines with a great many substances, particularly with acids.

Uses. Ammonia can be condensed to a liquid by the application of a moderate pressure. If the pressure is removed from

the liquid so obtained, this liquid rapidly passes again into the gaseous state, and in so doing absorbs a great deal of heat. Advantage is taken of this fact in the manufacture of ice. This is one of the main uses of ammonia. Large quantities of ammonia are also used in the manufacture of ammonium compounds such as ammonium chloride (NH_4Cl).

The manufacture of ice. Fig. 93 illustrates the method of manufacturing ice. The ammonia gas is liquefied in the pipes *A*, *B* by means of a compression pump. The pipes lead into a large brine tank, a cross section of which is shown in the figure. Into the brine (concentrated solution of calcium chloride) contained in this tank are dipped the vessels *D*, *E*, *F*, filled with pure water. The pressure is removed as it passes through the expansion valve *C* into the pipes immersed in the brine, and the heat absorbed by the rapid

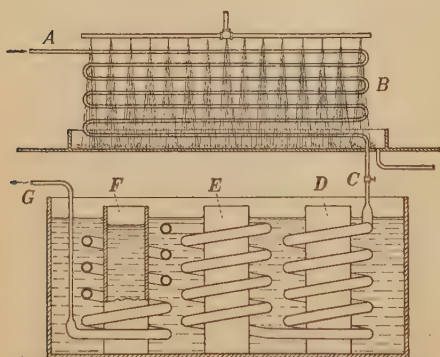
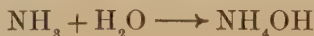


FIG. 93. Diagram illustrating the principle of an ammonia ice machine

evaporation of the liquid lowers the temperature of the brine below zero. The water in *D*, *E*, *F* is thereby frozen into cakes of ice. The gaseous ammonia resulting from the evaporation of the liquid escapes at *G* and is again liquefied, and the process is repeated.

Ammonium hydroxide (NH_4OH). The solution of ammonia in water, commonly called *aqua ammonia* or *ammonia water*, has strong basic properties. It turns red litmus blue and neutralizes acids, forming salts with them. It seems certain, therefore, that *when ammonia dissolves in water it combines chemically with the water* according to the equation



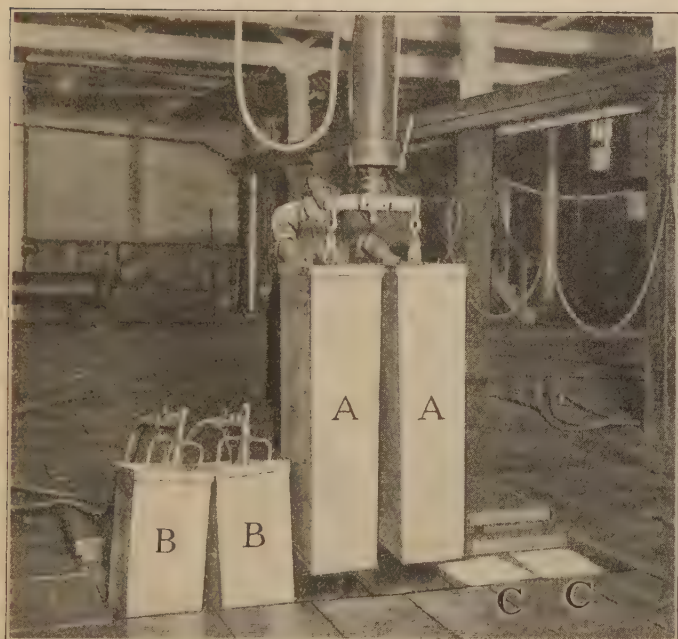


FIG. 94. View of the interior of an ice plant

The floor is made up of small wooden plates, each one forming the cover of one of the iron vessels in which the water is frozen. These vessels are immersed to their rim in the brine tank under the floor. The picture shows two of these vessels, *A, A*, being withdrawn from the brine. The water in these is frozen and the cakes of ice in them are removed by immersing the vessels for a short time in warm water and then inverting the vessels. The vessels are then filled with distilled water, again immersed in the brine, and left until the water is frozen. The picture also shows two vessels *B, B*, from which the ice has just been removed, being filled with water. As the water flows in through the hose at the top, the vessels gradually sink into the brine. The tops of two other vessels, *C, C*, are also shown. The water in these is frozen and the ice is ready to be withdrawn



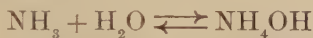
FIG. 95. View of the interior of a cold-storage plant

The temperature in a room may be kept very low by placing about the room strong iron pipes into which liquid ammonia is forced and allowed to vaporize. The vapor is then conducted away, compressed again to the liquid state, and then returned to the pipes in the cold-storage room, so that the process becomes continuous. Moisture in the air in such rooms freezes as it comes in contact with the pipes, so that the pipes are commonly surrounded by a layer of ice. By regulating the rate of evaporation of the liquid ammonia, any desired temperature (within limits) can be obtained. Since foods do not spoil when the temperature is kept down, it is possible in this way to store foods for a long period and to withdraw them as needed

The resulting compound, NH_4OH , called *ammonium hydroxide*, is a base just as sodium hydroxide is a base. The separation of the pure hydroxide from its solutions has not been accomplished, for as the solution becomes concentrated the compound decomposes again into ammonia and water:

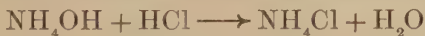


The solution of ammonia in water, therefore, constitutes a state of equilibrium between ammonia and water, on the one hand, and ammonium hydroxide, on the other. This condition is conveniently expressed in the following way:



Aqua ammonia is a good solvent for grease and is a familiar household article.

The ammonium radical. The univalent radical NH_4 plays the part of a metal in many chemical reactions, and is called *ammonium*. The ending *-ium* is given to the name to indicate the metallic properties of the substance, since the names of the metals in general have that ending. The salts formed by the action of the base ammonium hydroxide on acids are called *ammonium salts*. Thus, with hydrochloric acid, ammonium chloride (NH_4Cl) is formed, in accordance with the equation



ACIDS OF NITROGEN

The most important of the acids of nitrogen are the following: nitric acid (HNO_3) and nitrous acid (HNO_2).

Hydrogen nitrate (HNO_3). Hydrogen nitrate is very difficult to prepare because it is very unstable. It is always obtained in aqueous solution, and this solution constitutes ordinary *nitric acid*.

Nitric acid: properties. The concentrated nitric acid of commerce contains about 68 per cent of hydrogen nitrate and

32 per cent of water. Such a solution has a density of 1.4. When pure it is a colorless liquid, but it is frequently colored slightly brown owing to decomposition products.

Preparation. Nitric acid is ordinarily prepared in the laboratory by the action of sulfuric acid on sodium nitrate (NaNO_3), which occurs in large quantities in Chile. When

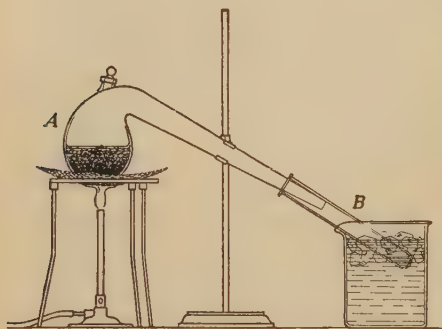


FIG. 96. Preparing nitric acid in the laboratory by the action of sulfuric acid on sodium nitrate

cold, concentrated sulfuric acid is poured upon sodium nitrate no chemical action seems to take place. If, however, the mixture is heated in a retort *A* (Fig. 96), nitric acid is given off as a vapor and may be easily condensed to a liquid by passing the vapor into a tube *B* surrounded by cold water. An

examination of the liquid left in the retort shows that it contains sodium hydrogen sulfate (NaHSO_4), only half of the hydrogen of sulfuric acid having been replaced by sodium. The reaction may be represented by the equation



Commercial preparation of nitric acid. In the United States nitric acid is prepared commercially by the same method that is used in the laboratory. Fig. 97 illustrates a form of apparatus used. Sodium nitrate and sulfuric acid are heated in the iron retort *A*. The resulting acid vapors pass in the direction indicated by the arrows and are condensed in the glass tubes *B*, which are covered with cloth kept cool by streams of water. These tubes are inclined so that the liquid resulting from the condensation of the vapors runs back into *C* and is drawn off into the large vessel *D*.

Preparation of nitric acid from the nitrogen of the air. Since the supply of sodium nitrate is gradually diminishing, many efforts have been made to find a way of making nitric acid from the nitrogen of the air. There are two general ways of doing this: (1) The first consists in exposing a mixture of nitrogen and oxygen to the action of an electrical discharge.

As a result certain oxides of nitrogen form which unite with water to form nitric acid. This method is used in Norway, where the water-falls make cheap electrical energy possible. (2) The better method consists in first converting the nitrogen

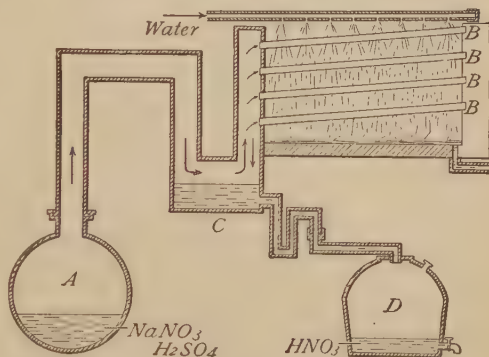


FIG. 97. A commercial still for the production of concentrated nitric acid

of the air into ammonia. This can be done either by the Haber process (p. 165) or by a process which will be described later under the heading "Cyanamide." If now the ammonia mixed with air is passed over a catalytic agent (platinum is used) in a heated tube, nitric acid is formed through the oxidizing action of the air, thus:



Nitric acid necessary for the manufacture of explosives. During the World War the Germans were driven off the seas and so could not obtain sodium nitrate (all of which comes from Chile) for the preparation of nitric acid. As a result they developed and used the ammonia process. The method is still largely used in Germany and to a limited extent in the United States and bids fair to come into general use at no very distant date.

Chemical conduct. The important reactions of nitric acid are as follows:

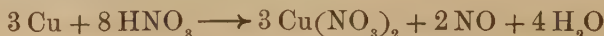
1. **Acid properties.** Nitric acid has all the characteristics of a strong acid, changing the color of indicators and forming salts with bases.

2. **Oxidizing action.** Nitric acid is not so stable as hydrochloric acid. When heated or when exposed for some time to the sunlight it undergoes partial decomposition, forming water and the two gases nitrogen dioxide and oxygen. Because of this property nitric acid is a good oxidizing agent. It acts upon the skin, turning it yellow.

3. **Action on metals.** When a metal reacts with nitric acid a salt of the acid is always formed. Hydrogen, however, is never evolved (except with a very dilute solution of acid) as in the case of hydrochloric acid, but in its place an oxide of nitrogen, generally nitric oxide (NO), is given off. The reason for this is as follows: At first thought we might expect that with the metals *above hydrogen* in the displacement series hydrogen would be evolved. If we recall, however, that hydrogen is a strong reducing agent and that nitric acid is a strong oxidizing agent, then it would seem reasonable that any hydrogen set free would not be evolved but, as fast as liberated, would act upon the nitric acid, forming water as indicated by the equation



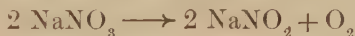
This is what actually happens. Metals *below hydrogen* in the displacement series ordinarily do not react with acids. Nitric acid, however, being a strong oxidizing agent, oxidizes the metals. A complex reaction takes place, however, as indicated in the following equation, which expresses the reaction between copper and nitric acid:



Aqua regia. Since nitric acid is a good oxidizing agent we might expect it to liberate chlorine from hydrogen chloride, and this is found to be the case. A mixture of 1 part of nitric acid by volume and 3 parts of hydrochloric acid is called *aqua regia* and is one of the strongest solvents known. *It owes its solvent powers not to its acid properties but to the nascent chlorine which it liberates.* Metals such as gold and platinum, which are not soluble in any of the common acids, readily dissolve in *aqua regia*, being converted into chlorides by the nascent chlorine.

Uses. Nitric acid has countless uses in the industries and in chemical laboratories. It is most extensively used in the manufacture of explosives of various kinds and of celluloid, photographic films, and dyes.

Salts of nitric acid: nitrates. The salts of nitric acid are called *nitrates*. Many of these salts will be described in the study of the metals. They are all soluble in water, and, when heated to a high temperature, undergo decomposition. In a few cases a nitrate, on being heated, evolves oxygen, forming a *nitrite*:



In other cases the decomposition goes farther, and the metal is left as oxide:



The nitrates are most largely used in the manufacture of gunpowder, sulfuric acid, nitric acid, and as a fertilizer.

Nitrous acid (HNO_2). It is an easy matter to obtain sodium nitrite (NaNO_2) by heating sodium nitrate, as explained in the previous paragraph. Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed, and nitrous acid is set free:



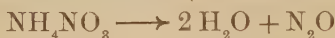
The acid is very unstable, however, and decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of dyes.

OXIDES OF NITROGEN

The most important of the oxides of nitrogen are the following:

Nitrous oxide (N_2O)		a colorless gas
Nitric oxide (NO)		a colorless gas
Nitrogen dioxide (NO_2)		a reddish-brown gas
Nitrogen trioxide (N_2O_3)		known only at low temperatures
Nitrogen pentoxide (N_2O_5)		a white solid

Nitrous oxide (laughing gas) (N_2O). This gas is most readily prepared by heating the solid known as ammonium nitrate:



It is colorless, is somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled, it produces a kind of hysteria (hence the name *laughing gas*) and, if taken in large amounts, insensibility to pain and unconsciousness. It was the first substance to be used as an anæsthetic in surgery, and it is still used in minor operations, such as those of dentistry.

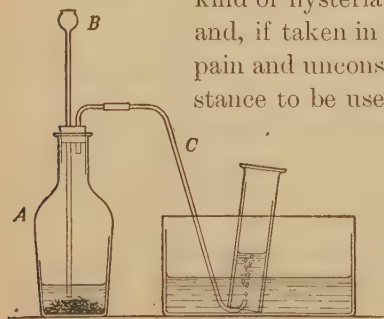
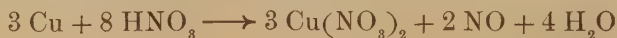


FIG. 98. The preparation of nitric oxide by the action of nitric acid on copper

Nitrous oxide is a very energetic oxidizing agent. Substances such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen,

forming oxides and setting free nitrogen. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

Nitric oxide (NO). Nitric oxide is most conveniently prepared by the action of nitric acid upon copper:



The metal is placed in the flask *A* (Fig. 98), and the acid added slowly through the funnel tube *B*. The gas escapes through *C* and is collected over water. Nitric oxide is a colorless gas slightly heavier than air. Unlike nitrous oxide, it does not part with its oxygen easily, and burning substances introduced into this gas are usually extinguished.

Nitrogen dioxide (NO_2). When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen, even at ordinary temperatures, forming a reddish-brown gas, NO_2 , which is called *nitrogen dioxide*:



It is a reddish-brown gas of unpleasant odor and is poisonous when inhaled.

To show the formation of nitrogen dioxide from nitric oxide and oxygen a tube is filled with the oxide, inverted in water, and pure oxygen is passed into it, as shown in Fig. 99. As each bubble of oxygen enters, it unites with the nitric oxide to form the reddish-brown

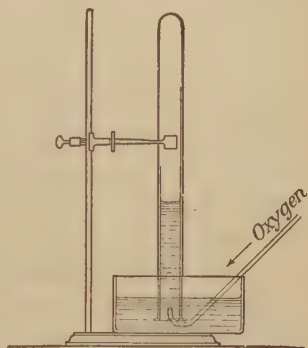


FIG. 99. The formation of nitrogen dioxide from nitric oxide and oxygen

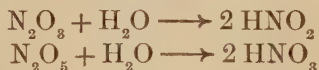
dioxide. In a few minutes the color fades (because of the action of water upon the dioxide) and the water slowly rises in the tube.

Nitrogen tetroxide. At lower temperatures nitrogen dioxide becomes paler in color and condenses to a pale-yellow liquid. It has been shown that this paler gas has the formula N_2O_4 and is called *nitrogen tetroxide*. At ordinary temperatures the gas is a mixture of the two, and we may express this relation thus:



Acid anhydrides. The oxides N_2O_3 (nitrogen trioxide) and N_2O_5 (nitrogen pentoxide) are rarely prepared and need not

be separately described. They bear a very interesting relation to the acids of nitrogen. When dissolved in water they combine with the water, forming acids:



Many other oxides act in the same way, combining with water to form an acid. Such oxides are called *acid anhydrides*.

Cyanogen (C_2N_2); hydrogen cyanide (HCN); hydrocyanic acid. At high temperatures carbon unites with nitrogen to form the colorless, very poisonous gas known as cyanogen (C_2N_2). With hydrogen and nitrogen it forms hydrogen cyanide (HCN), a colorless liquid boiling at 26° . Hydrogen cyanide vapor has the odor of peach kernels. *It is one of the most poisonous compounds known* and is used to destroy insects, especially those on citrous fruit trees, such as lemon and orange trees. When dissolved in water hydrogen cyanide forms a *very weak acid* known as *hydrocyanic acid* or *prussic acid*. Its salts are called cyanides. Sodium cyanide (NaCN) is a white solid, and its solution dissolves gold, hence it is used in extracting gold from its ores. The acid as well as its salts are all very poisonous.

EXERCISES

1. Give the formulas and names of all the gaseous compounds so far studied.
2. (a) What is a radical? (b) Give examples taken from the present chapter.
3. Perfectly dry ammonia gas does not affect litmus paper. Explain.
4. Why is nitric acid said to be a *strong* acid and ammonium hydroxide a *weak* base?
5. Sulfuric acid has a strong affinity for water. Could ammonia be dried by passing it through sulfuric acid?
6. Why is brine used in making artificial ice?
7. Distinguish between the terms *ammonium* and *ammonia*.

8. What is the valence of the ammonium radical?

9. Write the equations for the reaction taking place when ammonium hydroxide is neutralized by each of the three acids — hydrochloric, nitric, and sulfuric.

10. What are the properties of ammonia that make it suitable for the manufacture of artificial ice?

11. It is said that nitric acid is formed in the air during thunderstorms. Does this seem probable?

12. Discuss the energy changes which take place in the manufacture of artificial ice.

13. A stream of cold water is sprayed over the pipes *A*, *B* (Fig. 93), as shown in the figure. State the reason for this.

14. Why cannot nitric acid be used in the preparation of hydrogen, just as hydrochloric and sulfuric acids are used?

15. How could you easily distinguish between nitrous oxide and nitric oxide?

16. Are the poisonous properties of prussic acid due to its acid properties?

17. Why is the formula of cyanogen written C_2N_2 rather than CN ?

18. What compound of a metal is formed when it dissolves (*a*) in nitric acid? (*b*) in hydrochloric acid? (*c*) in aqua regia?

19. (*a*) How many liters of ammonia under standard conditions dissolve in 1 liter of water (p. 163)? (*b*) What weight of ammonium chloride will be required for its preparation?

20. (*a*) What is the density of the concentrated nitric acid of commerce (p. 168)? (*b*) What is the weight of 1 liter of this acid? (*c*) What weight of hydrogen nitrate does it contain?

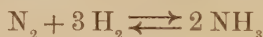
21. Suppose you wish to prepare 100 kilograms of the concentrated nitric acid of commerce. What compounds and what weight of each should you require for its preparation?

22. A chemist has an order from a dentist for 100 liters of nitrous oxide. What weight of ammonium nitrate will be necessary for its preparation?

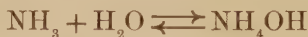
CHAPTER XIX

REVERSIBLE REACTIONS; EQUILIBRIUM

Reversible reactions. We have met with a number of reactions which are of a special interest because they can go in either direction. Thus, in the Haber process (p. 165) nitrogen and hydrogen combine to form ammonia; but ammonia, on the other hand, is decomposed into nitrogen and hydrogen when heated. The chemist expresses these facts in the following way:



Similarly, ammonia and water combine to form ammonium hydroxide (p. 167), while the latter compound is easily decomposed by heat into the compounds from which it is formed, thus:



Such reactions as the above, which may go in either direction, are known as *reversible reactions*.

Equilibrium. If we remember that the materials taking part in a reaction are made up of great numbers of molecules all of which are in rapid motion and are constantly changing their relations to each other, it is not difficult to see why some molecules should be decomposing while others are forming. *In time, however, a condition will be reached in which the changes in the one direction will just offset those in the other.* The *average* percentage of each material present will then remain unchanged. This condition of affairs is called *equilibrium*. Thus, in the Haber process ammonia, hydrogen, and nitrogen come to equilibrium when about 8 per cent of the nitrogen is combined to form ammonia.

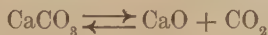
This principle of equilibrium may be illustrated by the movements of people in a busy town. In the early morning nearly everyone on the street is moving in one direction toward business. Presently an increasing number are moving in the reverse direction, and by the middle of the morning about as many move in one direction as in the other. The population of the town may then be said to have reached equilibrium between those who are at home and those at work in the town.

Mass action. Suppose, when equilibrium has been reached, we add an additional quantity of one of the acting substances—say hydrogen—in the case just mentioned. This will make it easier for the nitrogen to act upon the hydrogen, for the two kinds of molecules will now meet more frequently. It will not at all affect the rate at which ammonia is decomposing. The net effect will therefore be to bring about a new equilibrium in which a larger percentage of ammonia is present. *The effect produced by an excess of one of the reacting materials is called mass action.*

Changing an equilibrium to a completed reaction. If we withdraw the ammonia as fast as it is formed, before it has time to decompose, the reaction will go on until either the hydrogen or the nitrogen is used up. In the Haber process this is accomplished by absorbing the ammonia as fast as it is formed in water or dilute acids.

The point of equilibrium can therefore be changed or the equilibrium converted into a completed reaction by changing the acting mass of the substances taking part in the reaction.

Let us take another example. Ordinary limestone is impure calcium carbonate (CaCO_3). When heated it decomposes into the solid, calcium oxide (CaO), known as lime, and the gas, carbon dioxide. If heated in a closed vessel equilibrium is soon reached:



If heated in an open vessel, however, the carbon dioxide escapes as fast as formed and the reaction goes to completion.

Equilibrium in solution. In aqueous solution the molecules of an electrolyte keep parting into ions; while the ions, on meeting, recombine to form molecules, the result being an equilibrium between the two conditions, thus:



If we mix two electrolytes the equilibrium reached becomes much more complicated, for any positive ion may unite with any negative one. Thus, when we mix sodium nitrate and sulfuric acid in the preparation of nitric acid, we have present the ions Na^+ , NO_3^- , H^+ , and SO_4^{--} , together with the molecules NaNO_3 , Na_2SO_4 , NaHSO_4 , HNO_3 , and H_2SO_4 .

Completion of reactions in solution. The chemist makes use of reactions to secure various compounds in pure condition, and he wishes the yield to be as large as possible. Reactions which stop short of completion and end in an equilibrium are not suited to manufacturing purposes unless means can be found to break up the condition of equilibrium and bring the reaction to a definite conclusion. There are three conditions under which this may be accomplished.

1. *A volatile gas may be formed.* If the reaction is conducted under such conditions that one of the products is a gas *insoluble in the solvent*, the gas will make its escape as fast as it is formed, and this action will continue until one or the other of the ions taking part in its formation is used up.

Thus, when we mix sulfuric acid and sodium nitrate (p. 168) no visible reaction takes place. But if we heat the mixture above the boiling point of nitric acid, then the nitric acid formed in the equilibrium between the H^+ and the NO_3^- ions is converted into a gas *insoluble in sulfuric acid* and distills away until the NO_3^- ions are used up. We then have a completed reaction expressed in the equation

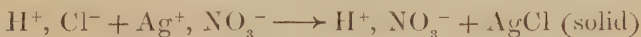


It is in this way that most acids are prepared. Their salts are heated with some acid of high boiling point, usually with sulfuric acid, which boils at 338°.

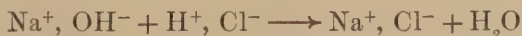
2. An insoluble solid may be formed. When hydrochloric acid (HCl) and silver nitrate (AgNO_3) are brought together in solution we have in addition to these two compounds the ions H^+ , Cl^- , Ag^+ , NO_3^- and the new combinations HNO_3 and AgCl . One of these, namely, silver chloride (AgCl), is insoluble in water; therefore as fast as it is formed, it separates from the solution as a curdy white precipitate (Fig. 100). The reaction therefore continues till either the Ag^+ or the Cl^- is used up, the completed equation being



FIG. 100. Precipitating silver chloride by the action of hydrochloric acid on silver nitrate



3. Two different ions may unite to form an un-ionized molecule. When we bring together sodium hydroxide and hydrochloric acid in solution, we have the ions H^+ , Cl^- , Na^+ , and OH^- . The H^+ ions and the OH^- ions unite to form molecules of water *which do not again part into ions* save to a very slight extent. This leaves only the ions of NaCl in solution, the equation being



Neutralization is practically a completed reaction *because water is so little ionized.*

EXERCISES

1. If the quantity of any substance (say the water in a pond or the money in a bank) remains constant, does this necessarily prove that the substance is undergoing no change? Give other examples to illustrate this same principle.

2. Give examples of equilibrium other than those mentioned in this chapter.

3. Suggest conditions for making the reaction represented below go in either direction :



4. In the preparation of nitric acid (p. 168) why do we heat the mixture of sodium nitrate and sulfuric acid?

5. (a) In the preparation of hydrochloric acid is it necessary to apply heat? (b) Why?

6. Why is heat unnecessary in preparing carbon dioxide from marble and hydrochloric acid?

7. Suppose you were to heat some water in a strong closed vessel to 2500° ; represent the changes taking place in the water at this temperature (p. 67).

8. What reactions should you expect to take place when solutions of silver nitrate and sodium chloride are mixed?

9. Barium sulfate (BaSO_4) is a white insoluble compound much used in paints. Suppose you had a supply of barium chloride (BaCl_2) and wished to convert it into barium sulfate. Suggest two methods (different in principle) for doing this.

10. The use of sulfuric acid in preparing other acids, such as nitric and hydrochloric, is based on what property of the acid?

CHAPTER XX

SULFUR AND ITS COMPOUNDS

Introduction. While sulfur is not to be regarded as one of the more abundant elements, yet it has been known from the earliest times and, indeed, was one of the favorite substances of the alchemists, who thought that all metals were made up of mercury and sulfur and that by changing the proportions one metal could be converted into another. Biblical writers were certainly familiar with sulfur, for we read of "the lake burning with fire and brimstone."

Properties. Sulfur occurs in a variety of forms: The ordinary form is a pale-yellow crystalline solid without taste and with but a faint odor. It is insoluble in water, but is freely soluble in a few liquids, notably in carbon disulfide. It melts when heated and forms a rather thin, straw-colored liquid. As the temperature is raised, this liquid turns darker in color and becomes thicker, until at about 235° it is almost black and is so thick that the vessel containing it can be inverted without danger of the liquid's running out. At higher temperatures it becomes thin once more and boils at 444.6° , forming a yellowish vapor. When the vapor cools the same changes take place in reverse order.

Occurrence. Sulfur is widely distributed in nature and occurs in large quantities in the uncombined form, especially in the neighborhood of volcanoes. Sicily has long been famous for its sulfur mines, and in more recent years large deposits have been found in Louisiana and Texas. It is occasionally found in well-formed crystals (Fig. 101).

In combination, sulfur occurs abundantly combined with metals; in smaller amounts it is found in a great variety of minerals and is a constituent of many vegetable and animal substances, especially of the yolk of eggs.

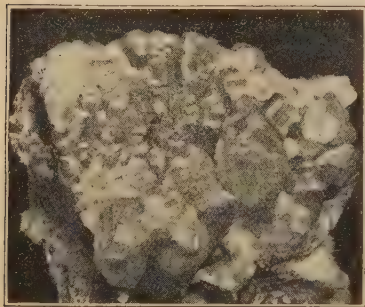


FIG. 101. Crystals of rhombic sulfur as they are found in nature

Extraction of sulfur. In Louisiana and Texas the sulfur occurs in deposits far underground and is covered with quicksand so that it cannot be mined. One of these deposits lies at a depth of 700 feet, is circular in shape, and is about half a

mile in diameter and 500 feet in thickness. Wells are drilled into the deposit, and superheated water (above 160°) is forced down through suitable pipes. The hot water not only melts the sulfur but, being under pressure, forces the molten sulfur to the



FIG. 102. Forcing liquid sulfur from deep wells in Louisiana by means of hot water under pressure

earth's surface through pipes suitably arranged (A, Fig. 102). The liquid sulfur then solidifies in very large blocks. A single well has produced 500 tons daily, and the product is 99.5 per

cent pure. Practically all the sulfur used in the United States comes from the Louisiana and Texas deposits.

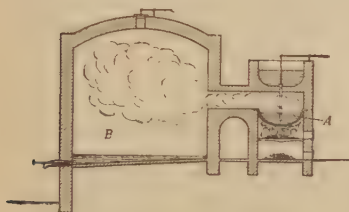


FIG. 103. A sulfur still

Distillation of sulfur. Sulfur may be distilled by heating it in a retort-shaped vessel *A* (Fig. 103), the exit tube of which opens into a cooling chamber *B* of brickwork.

When the sulfur vapor first enters the cold chamber it condenses as a fine crystalline powder called *flowers of sulfur* (Fig. 104). As the condensing chamber becomes warm the sulfur condenses as a liquid and is drawn off into cylindrical molds, the product being called *roll sulfur* or *brimstone* (Fig. 104).

Varieties of sulfur. Sulfur exists in a number of quite different (allotropic) forms. Many other elements occur in a number of different forms, but those of sulfur are unusually numerous and are easy to obtain. The best-known are the following :

1. *Ordinary, or rhombic, sulfur.*

When sulfur crystallizes from solution in liquids (notably from carbon disulfide) it is obtained in compact yellow crystals which melt at 112.8° . This is called *rhombic sulfur* (Fig. 101), and brimstone is composed largely of this variety.

2. *Prismatic, or monoclinic, sul-*

fur. When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the



FIG. 104. Two common forms of sulfur

vessel is in the form of fine needle-shaped crystals which melt at 119.2° . The needle-shaped form is called *monoclinic sulfur*. At all temperatures below 96° the needle-shaped crystals break up more or less rapidly into little crystals of the rhombic variety.

3. Plastic sulfur. When boiling sulfur is poured into cold water it assumes a gummy, doughlike form which is quite elastic. It is simply undercooled liquid sulfur. It is easily

made by distilling sulfur from a small, short-necked retort (such as is represented in Fig. 105) and allowing the liquid to run directly into water. In a few days it passes over into ordinary rhombic sulfur.

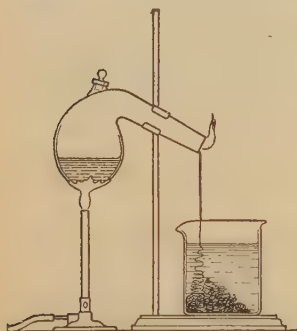


FIG. 105. The preparation of plastic sulfur

Chemical conduct of sulfur. Sulfur burns in oxygen or in the air with a pale-blue flame, forming sulfur dioxide (SO_2). Most metals when heated with sulfur combine directly with it, forming metallic sulfides. In some cases the action

is so energetic that the mass becomes incandescent, as is the case with iron. This conduct recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine with sulfur.

Uses of sulfur. Large quantities of sulfur are used in the manufacture of gunpowder, vulcanized rubber, sulfuric acid, and other compounds of the element. It is also used extensively in the manufacture of insecticides for use in orchards and vineyards.

Lime-sulfur spray. The chief sulfur insecticide is known as *lime-sulfur spray*. It is made by boiling sulfur with slaked lime, by which process a deep-red liquor is obtained, consisting essentially of a solution of sulfides of calcium (CaS_4 and CaS_5).

The liquid is a very efficient insecticide, particularly for scale, and it is also a fungicide. Large quantities of it are used for spraying fruit trees (Fig. 106).

Hydrogen sulfide (H_2S): properties. Sulfur forms with hydrogen the important compound known as hydrogen sulfide (H_2S). This is a colorless gas having a weak, disagreeable taste and a most offensive odor, suggesting rotten eggs. At ordinary

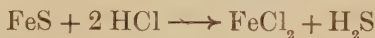


FIG. 106. Spraying an orchard of fruit trees with lime-sulfur spray

temperatures it is but sparingly soluble in water; in boiling water it is not soluble at all. When inhaled in concentrated form it acts as a violent poison, and even when much diluted with air produces headache, dizziness, and nausea. It is 1.18 times as heavy as air.*

Occurrence. Hydrogen sulfide is found in the vapors issuing from volcanoes. It also occurs in solution in many natural waters (*sulfur waters*). It is formed when organic matter containing sulfur undergoes decay, just as ammonia is formed from nitrogenous matter.

Preparation. Since hydrogen sulfide is a gas which is but little soluble in water, it can be prepared *by treating a sulfide with an acid* (p. 179). Iron sulfide (FeS) is usually employed:



A convenient apparatus is shown in Fig. 107. A few lumps of iron sulfide are placed in the bottle *A* and dilute acid is added a little at a time through the funnel tube *B*, the gas escaping through the tube *C*.

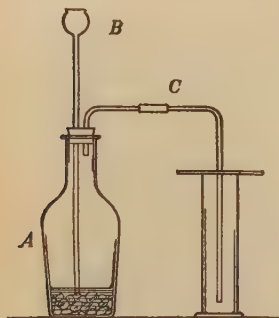
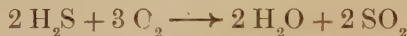


FIG. 107. The preparation of hydrogen sulfide by the action of hydrochloric acid on sulfide of iron

Chemical conduct. The most important chemical properties of hydrogen sulfide are the following:

1. **Acid properties.** When dissolved in water, hydrogen sulfide acts as a weak acid, the solution being sometimes called *hydrosulfuric acid*. The solution turns blue litmus red and neutralizes bases, forming salts called *sulfides*.

2. **Action with oxygen.** The elements composing hydrogen sulfide have each a strong tendency to combine with oxygen and are not held together very firmly. Consequently the gas burns readily in oxygen or air according to the equation



When there is not enough oxygen for both the sulfur and the hydrogen or when the temperature is kept low, the latter element combines with the oxygen, and the sulfur is set free:



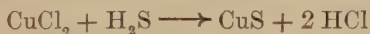
3. **Reducing action.** Owing to the ease with which hydrogen sulfide decomposes, and the strong tendency of both sulfur and hydrogen to combine with oxygen, the substance is a strong *reducing agent*.

4. **Action on metals.** Hydrogen sulfide acts upon many metals, forming *sulfides*. Silver sulfide (Ag_2S) is black, and it is owing to traces of hydrogen sulfide in the air that silver objects tarnish.

Sulfur waters. The waters of many natural springs hold hydrogen sulfide in solution, as is indicated by their strong odor and the way in which they will blacken a silver coin. When the water reaches the air the hydrogen sulfide is slowly oxidized, with the liberation of sulfur, which often deposits about the borders of the spring.

Salts of hydrosulfuric acid ; sulfides. The salts of hydrosulfuric acid (called *sulfides*) form an important class of compounds. Many of them are found abundantly in nature, and some of them are important ores.

Uses of the sulfides in analysis. Most of the sulfides are insoluble in water, and some of them are insoluble in acids. Consequently, when hydrogen sulfide is bubbled through a solution of a salt, it often happens that a sulfide is precipitated. With copper chloride the equation is



Because of the fact that some metals are precipitated in this way as sulfides, while others are not, hydrogen sulfide is extensively used in the separation of the metals in the laboratory.

Laboratory preparation of sulfides. In the laboratory the sulfides are prepared by passing hydrogen sulfide through solutions of the salts of the metals as shown in Fig. 108. The hydrogen sulfide generated in flask *A* is passed through bottles *B* and *C*, containing, say, solutions of silver nitrate and arsenic chloride respectively. As the gas bubbles through the solutions there is formed black silver sulfide in *B* and yellow arsenic sulfide in *C*.

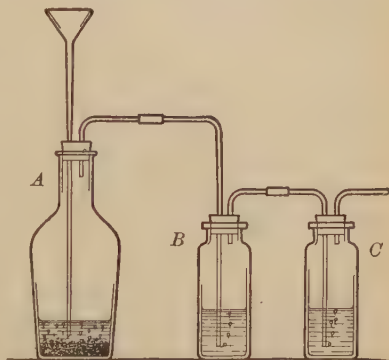


FIG. 108. The preparation of insoluble sulfides in the laboratory

OXIDES OF SULFUR

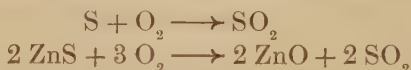
Sulfur forms two well-known compounds with oxygen: sulfur dioxide (SO_2), sometimes called *sulfurous anhydride*; and sulfur trioxide (SO_3), frequently called *sulfuric anhydride*.

Sulfur dioxide: properties. Sulfur dioxide is a colorless gas which at ordinary temperatures is 2.2 times as heavy as air. It has a peculiar, irritating odor. The gas is very soluble in water, 1 volume of water dissolving 80 volumes of the gas under standard conditions. It is easily condensed to a colorless liquid and can be purchased in this condition, stored in strong bottles or in metal cylinders.

Occurrence. Sulfur dioxide often occurs in nature in the gases issuing from volcanoes, and in solution in the water of many springs. It is likely to be found wherever sulfur compounds are undergoing oxidation.

Preparation. Two general ways may be mentioned for the preparation of sulfur dioxide:

1. *By the combustion of sulfur.* Sulfur dioxide is readily formed when sulfur or certain compounds containing sulfur, such as the metal sulfides, are heated in air or oxygen:



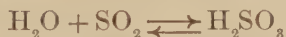
2. *By the reduction of sulfuric acid.* When concentrated sulfuric acid is heated with certain metals, such as copper, part of the acid is changed into copper sulfate and part is reduced to sulfurous acid, the latter decomposing into sulfur dioxide and water. The details of the reaction will be given later, but the complete equation is as follows:



Chemical conduct. Sulfur dioxide has a marked tendency to combine with other substances and is therefore an active substance chemically. It combines with oxygen gas, but not very

easily. It can, however, take oxygen away from some other substances and is therefore a good reducing agent. Its most marked chemical property is its ability to combine with water.

Sulfurous acid (H_2SO_3). When sulfur dioxide is passed into water it combines chemically with it to form *sulfurous acid* (H_2SO_3). It is impossible to prepare this acid in pure form, as it breaks down very easily into water and sulfur dioxide. The reaction is therefore reversible and is expressed by the equation



Solutions of the acid in water are often prepared and have a number of interesting properties and commercial uses.

1. **Acid properties.** The solution has all the properties of a very weak acid. When neutralized by bases, sulfurous acid yields salts called *sulfites*, most of which are insoluble in water.

2. **Reducing properties.** Solutions of sulfurous acid act as good reducing agents. This is due to the fact that sulfurous acid has the power of taking up oxygen from the air or from substances rich in oxygen, and is changed by this reaction into sulfuric acid:

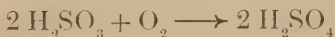


FIG. 109. Bleaching a red flower with sulfurous acid

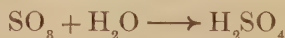
3. **Bleaching properties.** Sulfurous acid has bleaching properties, although it is not as good a bleaching agent as chlorine (p. 140). It is used, however, to bleach substances that would be injured by the action of chlorine, such as paper, straw goods, and even such foods as canned corn and dried fruits. As a rule the bleaching is not permanent.

The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 109) in which has been placed some highly colored flower moistened with water. Straw hats may be cleaned and brightened in a similar way.

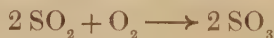
Uses of sulfurous acid. Sulfurous acid is used as a bleaching agent, as noted above. It also is used in certain foods and sirups, serving not only as a bleaching agent but also as a preservative. Whether or not its use in foods should be permitted has been a much-debated question.

Salts of sulfurous acid; sulfites. The sulfites are solid compounds and, like sulfurous acid, have the power of taking up oxygen very readily and are good reducing agents. On account of this tendency commercial sulfites are often contaminated with sulfates.

Sulfur trioxide (SO_3): properties. Sulfur trioxide is a colorless liquid which solidifies at about 15° and boils at 46° . A trace of moisture causes it to solidify into a mass of silky white crystals which have the formula S_2O_6 . In contact with the air it fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulfuric acid, so that sulfur trioxide is the *anhydride* of that acid (p. 174):



Preparation. When sulfur dioxide and oxygen are heated together at a rather high temperature, a small amount of sulfur trioxide (SO_3) is formed, but the reaction is slow and incomplete. If, however, a suitable catalytic agent is present, the reaction is rapid and nearly complete:



Experimental preparation of sulfur trioxide. The experiment can be performed by the use of the apparatus shown in Fig. 110. The catalytic agent (fine platinum) is secured by moistening asbestos fiber with a solution of chloroplatinic acid and igniting it in a flame. The fiber, covered with fine platinum, is placed in a tube of hard glass *A*, which is then heated with a burner to about 400° , while sulfur dioxide and air are passed into the tube through the drying bottles *B* and *C*. Union takes place at once, and the

strongly fuming sulfur trioxide escapes from the jet at the end of the tube, and may be condensed by surrounding the receiving tube *D* with a freezing mixture.

Sulfuric acid (oil of vitriol) (H_2SO_4). Strictly speaking, sulfuric acid is a solution of hydrogen sulfate (H_2SO_4) in water. It is customary, however, to apply the term *sulfuric acid* to both the hydrogen sulfate and its aqueous solution. The pure compound is a colorless, oily liquid nearly twice as heavy as

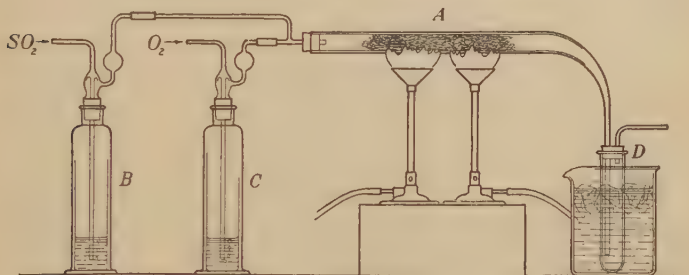


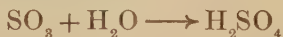
FIG. 110. The preparation of sulfur trioxide

water. The ordinary concentrated acid contains about 2 per cent of water, has a density of 1.84, and boils at 338° . It is sometimes called *oil of vitriol*, since it was formerly made by distilling a mixture of substances, one of which was called *green vitriol*.

Sulfuric acid is one of the most important of all manufactured chemicals. Indeed, it has been said that the state of civilization of a country can be told by the quantity of sulfuric acid used, but such a statement, while probably true, could be just as well made in regard to a number of substances, such as sodium hydroxide or soap. Enormous quantities of the acid are used in many of the industries, especially in dissolving off the scale from metals, in the refining of petroleum, and in the manufacture of explosives, dyes, hydrochloric and nitric acids, sodium carbonate, and phosphate fertilizers. It is one of the most common laboratory reagents.

Manufacture of sulfuric acid. Sulfuric acid can be made at low cost and is the cheapest of the commercial acids. Two general methods are used in its manufacture:

1. **Contact process.** In this process sulfur trioxide is made from sulfur dioxide and oxygen, as explained under Fig. 110. The two gases are conducted through iron tubes filled with some porous material, such as asbestos or sodium sulfate, through which is interspersed a suitable catalyzer, such as iron oxide or platinum. The sulfur trioxide so formed reacts with water to form sulfuric acid:



The contact process is used only when the *concentrated* acid is desired.

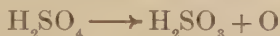
2. **Chamber process.** The older method of manufacture, exclusively employed until recent years and still the most important process, is much more complicated. The conversion of water, sulfur dioxide, and oxygen into sulfuric acid is accomplished by the catalytic action of oxides of nitrogen. Since these oxides are gases it is difficult to prevent their escape, and very elaborate precautions have to be taken to reduce the loss as much as possible. The reactions are brought about in very large lead chambers into which oxides of nitrogen, sulfur dioxide, steam, and air (to furnish oxygen) are introduced in suitable proportions.

The dilute acid which collects upon the floor of the lead chambers contains from 62 to 70 per cent of hydrogen sulfate. It is drawn off and in this form serves for many purposes, such as the manufacture of fertilizers. The pure concentrated acid can be prepared from the dilute acid by distillation, but the process is costly, so that it is sometimes cheaper to prepare this form of acid by the contact process.

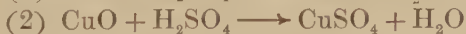
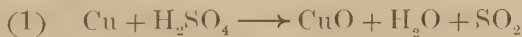
Chemical conduct. Sulfuric acid possesses properties which make it one of the most important of chemical substances.

1. *Action as an acid.* In dilute solution sulfuric acid acts as a very strong acid, turning blue litmus red and forming salts with oxides and hydroxides.

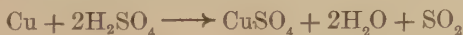
2. *Action as an oxidizing agent.* Sulfuric acid contains a large percentage of oxygen and, like nitric acid, is a very good oxidizing agent. When the concentrated acid is heated with sulfur or carbon or various other substances, oxidation takes place, the sulfuric acid decomposing according to the equation



3. *Action on metals.* Dilute sulfuric acid acts on the metals above hydrogen in the displacement series, forming salts of the acid (*sulfates*) and liberating hydrogen (p. 33). The *concentrated* acid, being a good oxidizing agent, acts in a different way upon the metals above hydrogen in the displacement series, as well as upon most of the metals below hydrogen. The metal is first oxidized by the acid; the resulting oxide then reacts with more of the acid, forming a salt and water. Thus, with copper the equations are



By canceling the formula of copper oxide in the above equations (since the oxide is produced in the first reaction and consumed in the second) we may combine the two equations into a single one; namely,



This equation tells us what materials are used up and what the final products are; it does not tell us what materials may have been produced and consumed in the process.

4. *Action on salts.* We have repeatedly seen that an acid of high boiling point heated with the salt of some acid of lower boiling point will drive out the low-boiling acid (p. 179).

The boiling point of sulfuric acid (338°) is higher than that of almost any common acid; hence it is largely used in the preparation of other acids.

5. Action on water. Concentrated sulfuric acid has a very great affinity for water and is therefore an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by bubbling them through the concentrated acid.

Not only can sulfuric acid absorb water but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even flesh, all of which contain much oxygen and hydrogen in addition to carbon, are charred by the action of the concentrated acid.

Salts of sulfuric acid; sulfates. The sulfates form a very important class of salts, and many of them have commercial uses. *Copperas* (iron sulfate), *blue vitriol* (copper sulfate), and *Epsom salt* (magnesium sulfate) serve as examples. Many sulfates are important minerals, prominent among these being *gypsum* (calcium sulfate) and *barite* (barium sulfate).

Monobasic and dibasic acids. Acids like hydrochloric and nitric acids, which have only one replaceable hydrogen atom in the molecule (or, in other words, which yield one hydrogen ion in solution), are called *monobasic acids*. Acids like sulfuric acid, which have two replaceable hydrogen atoms in each molecule, are called *dibasic acids*. Similarly, we may have *tribasic* and *tetrabasic acids*.

Normal and acid salts. It is possible for such acids as H_2S , H_2SO_3 , and H_2SO_4 to form two kinds of salts. In the one all the hydrogen of the acid has been replaced by a metal, as in the salts Na_2S and Na_2SO_4 . These are called *normal salts*. In the other only one half of the hydrogen has been replaced, as in the salts NaHS and NaHSO_4 . These are called *acid salts*, since

they are at once both salts and acids. Acid salts are often designated by the prefix *bi-*; thus, NaHSO_4 is called sodium bisulfate, sodium acid sulfate, or sodium hydrogen sulfate.

Carbon disulfide (CS_2). When sulfur vapor is passed over highly heated carbon the two elements combine, forming *carbon disulfide* (CS_2), just as oxygen and carbon unite to form carbon dioxide (CO_2). The substance is a heavy, colorless liquid possessing, when pure, a pleasant odor. On standing, especially when exposed to sunlight, it undergoes a slight decomposition and acquires a most disagreeable odor. *It is a very good solvent for many substances, such as gums, rubber, waxes, and fats, which are insoluble in most liquids.* It boils at a low temperature (46°), and its vapor is not only very poisonous but is very inflammable. It is prepared in considerable quantities for use as a solvent and as an insecticide.

EXERCISES

1. What elements so far studied occur in different allotropic forms?
2. Suppose you were to grind a part of a stick of brimstone to a fine powder. Would the powder and the stick be allotropic forms of sulfur?
3. How could you tell whether any two forms of sulfur are allotropic forms or simply different physical states of the same form?
4. Why were the ancients so familiar with sulfur?
5. The reaction used in preparing hydrogen sulfide in the laboratory is a reversible one. Why does it ordinarily complete itself?
6. If hydrogen sulfide were a liquid, could we use the ordinary method of preparation?
7. Hydrogen sulfide is said to be as poisonous as carbon monoxide, and yet we do not fear it as we do carbon monoxide. Why?
8. Do sulfur waters contain free sulfur?
9. (a) What foods contain sulfur? (b) Why do such foods blacken silver spoons in contact with them?
10. Enumerate the different reactions so far studied in which catalytic agents have been employed.

11. Can you suggest any reason why sulfur dioxide is so much more soluble in water than is oxygen or nitrogen?

12. How should you expect dilute sulfuric acid to act (a) upon iron? (b) upon silver? (See displacement series.)

13. Zinc dissolves in both dilute and concentrated sulfuric acid. (a) What compound of the metal forms in each case? (b) What gas is evolved in each case?

14. What reaction should you expect to take place if hydrogen sulfide were passed into a solution of sodium hydroxide?

15. (a) Define each of the following terms: acid, salt, monobasic acid, tribasic acid, normal salt, acid salt. (b) Give an example of each.

16. State what compound a metal would form when dissolved in each of the following: hydrochloric acid, nitric acid, sulfuric acid, aqua regia.

17. When carbon disulfide burns, the two elements present form the oxides CO_2 and SO_2 . Write the equation for the reaction.

18. (a) The compound Na_2SO_3 is a salt of what acid? (b) When this salt is brought in contact with sulfuric acid, sulfur dioxide is evolved; account for its formation.

19. The common powders sold for cleaning straw hats contain sodium sulfite. Upon what property does its cleaning action depend?

20. What volume of oxygen would be required to burn completely 100 liters of hydrogen sulfide? (Note that both hydrogen sulfide and oxygen are gases. See p. 115.)

21. Calculate the percentage composition of hydrogen sulfate.

22. During the World War one plant produced daily 1000 tons of sulfuric acid containing 60 per cent of hydrogen sulfate. What was the daily consumption of sulfur in this plant, assuming that none was lost in the process?

23. What weight of carbon disulfide can be made from 100 kilograms of sulfur?

CHAPTER XXI

THE PERIODIC LAW

A number of the elements have now been studied somewhat closely. Of these oxygen, hydrogen, nitrogen, carbon, chlorine, and sodium have almost no point of similarity as regards their chemical conduct. On the other hand, oxygen and sulfur, while quite different physically, have much in common in the way they act toward other chemicals.

Eighty-seven elements are now known. If all these should have properties as diverse as do oxygen, hydrogen, nitrogen, carbon, chlorine, and sodium, the study of chemistry would plainly be very difficult and complicated. Fortunately a study of the elements shows that certain ones resemble each other more or less closely, so that it is possible to arrange them in groups and then study the group as a whole. A number of different methods for classifying the elements have been suggested, but the one advanced in 1869 by the Russian chemist Mendeléeff (Fig. 111) has proved the most fruitful. In accordance with this method *the elements are arranged in groups or periods, according to their atomic weights.*

The periodic grouping. The general arrangement suggested by Mendeléeff and extended so as to include elements more recently discovered is as follows: Omitting hydrogen, which has the smallest atomic weight, and beginning with helium, which has an atomic weight of 4.00, the succeeding seven elements are arranged in a horizontal row in the order of their atomic weights, as given below. These eight elements all differ markedly from each other, but neon, the one having the next highest atomic weight, is very similar to helium.

It is placed just under helium, and a new horizontal row follows, as shown below. The element following chlorine, namely, argon, resembles helium and neon and begins a third row.

He (4.00)	Li (6.94)	Cl (9.1)	B (10.9)	C (12.005)	N (14.008)	O (16)	F (19)
Ne (20.2)	Na (23)	Mg (24.32)	Al (27.1)	Si (28.3)	P (31.04)	S (32.06)	Cl (35.46)
A (39.90)	K (39.1)	Ca (40.07)	Sc (45.1)	Ti (48.1)	V (51)	Cr (52)	Mn (54.93)

If now we consider the elements that fall under each other in these three rows, a remarkable fact is brought to light.

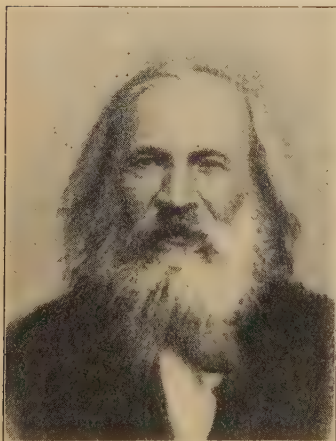


FIG. 111. Mendeléeff (1834-1907)

A Russian chemist who proposed the periodic classification of the elements

Not only is there a strong similarity between helium, neon, and argon, which form the first vertical column, *but the elements in the other columns exhibit much of the same kind of similarity among themselves and evidently form natural groups.*

Iron, nickel, and cobalt, following manganese, have atomic weights near together and are very similar chemically. They do not strongly resemble any of the elements so far considered and so are placed in a group by themselves. The first three horizontal rows of the table (p. 199) show the arrangement

of these twenty-seven elements. A new horizontal row is begun with copper. Following the fifth and seventh rows are groups of three closely related elements, so the completed arrangement has the appearance represented in the table.

Relation of properties of elements to atomic weights. There is evidently a close relation between the properties of an element and its atomic weight. For example, consider the elements in the first horizontal row. Helium is an inert element. Following

THE PERIODIC ARRANGEMENT OF THE ELEMENTS AND THE ATOMIC NUMBERS

Type of hydride	RH	RH ₂	RH ₃	RH ₄	RU ₃	RU ₃	RU ₃	RU ₂	RH	
Type of oxide	R ₂ O	RO	RO ₂	RO ₂	RO ₂	R ₂ O ₃	RO ₃	RO ₃	R ₂ O ₇	RO ₄
PERIODS	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII		
1	2 He = 4.0	3 Li = 6.94	4 Be = 9.01	5 B = 10.8	6 C = 12.005	7 N = 14.008	8 O = 16.0	9 F = 19.0		
2	10 Ne = 20.2	11 Na = 23.0	12 Mg = 24.32	13 Al = 27.1	14 Si = 28.3	15 P = 31.0	16 S = 32.06	17 Cl = 35.46		
3	18 Ar = 39.9	19 K = 39.1	20 Ca = 40.07	21 Sc = 45.1	22 Ti = 48.1	23 V = 51.0	24 Cr = 52.0	25 Mn = 54.93	26 Fe = 55.84	27 Co = 58.97
4	29 Cu = 63.57	30 Zn = 65.37	31 Ga = 70.1	32 Ge = 72.5	33 As = 74.96	34 Se = 79.2	35 Br = 79.92			28 Ni = 58.69*
5	36 Kr = 83.92	37 Rb = 85.45	38 Sr = 87.63	39 Y = 89.33	40 Zr = 91.5	41 Nb = 92.9	42 Mo = 95.9	43 Ru = 101.7	44 Rh = 102.9	45 Pd = 106.7
6	47 Ag = 107.88	48 Cd = 112.4	49 In = 114.8	50 Sn = 118.7	51 Sb = 120.2	52 Te = 127.5	53 I = 126.92			
7	54 Xe = 136.2	55 Ba = 137.37	56 La = 139.0*	57 Ce = 140.25	58 Pr = 140.9	59 Nd = 144.2	60 Pm = 145.0	61 Sm = 150.4	62 Eu = 151.96	63 Gd = 157.25
8	79 Au = 197.2	80 Hg = 200.6	81 Tl = 204.0	82 Pb = 207.2	83 Bi = 208.98	84 Po = 209	85 At = 210			
9	86 Rn = 222.4	87 Fr = 223	88 Ra = 226.0	89 Ac = 227	90 Th = 232.04	91 Pa = 231.04	92 U = 238.03			

* Following lanthanum occurs a series of elements, known as the rare earth elements, of atomic numbers 58-72. Of these, number 61 is unknown. They all closely resemble lanthanum and so cannot be distributed among the several groups. Cerium has some properties that seem to place it in Group IV. The newly discovered element hafnium appears to be number 72 and also belongs in Group IV, just before tantalum.

it, lithium is a metallic element, has a valence of 1, and possesses a strong base-forming character. The next element, glucinum, has a valence of 2 and is less strongly base-forming, while boron has some base-forming and some acid-forming properties. In carbon all base-forming properties have disappeared, and the acid-forming properties are more marked than in boron. These become still more emphasized as we pass through nitrogen and oxygen, until, on reaching fluorine, we have one of the strongest acid-forming elements. *The properties of these eight elements vary regularly with their atomic weights* or, in mathematical language, are *regular functions* of them.

The periodic law. If it were true that helium had the smallest atomic weight of any of the elements and fluorine the greatest, so that in passing from one to the other we included all the elements, we could say that the properties of elements were *regular functions* of their atomic weights. But fluorine is an element of relatively small atomic weight, and the one following it, neon, breaks the regular order, for in it reappear all the characteristic properties of helium. Sodium, following neon, bears much the same relation to lithium that neon does to helium, and the properties of the elements in the second row vary much as the properties of the elements in the first row did, until argon is reached, when another repetition begins. The properties of the elements do not vary *continuously*, therefore, with atomic weights, but at regular intervals there is a repetition, or *period*. This generalization is known as the *periodic law* and may be stated thus: *The properties of elements are periodic functions of their atomic weights.*

Two families in a group. The elements of each group (excepting Group 0) fall naturally into two families. The elements in the odd-numbered horizontal rows, or periods, form one family, those in the even-numbered periods the other. In the table these are arranged under the headings *A* and *B*. The elements in one family are much more similar to each

other than they are to those in the other family in the same group. Thus, magnesium, zinc, cadmium, and mercury form one family of very similar elements in Group II, while glucinum, calcium, strontium, barium, and radium form the other.

Family resemblances. Let us inquire more closely in what respects the elements of a family resemble each other.

1. *Valence.* In general the highest valence of the elements in a family is the same, and the formulas of their compounds are therefore similar. The formulas R_2O , RO , etc., placed below the columns, represent the oxides of the elements in the column, while the formulas RH , RH_2 , etc. represent the hydrides or chlorides, in which R represents any one of the elements of the family.

2. *Chemical conduct.* The chemical characteristics of the members of a family are somewhat similar. If one member is a metal, the others usually are; if one is a nonmetal, so, too, are the others. There is also a certain regularity in the conduct of the elements in each family.

3. *Physical properties.* In the same way, the physical properties of the members of a family are in general somewhat similar and show a regular gradation as we pass from element to element in the family.

Value of the periodic law. The periodic law has proved of much value in the development of the science of chemistry.

1. *It simplifies study.* It is at once evident that such regularities very much simplify the study of chemistry. A thorough study of one element of a family makes the study of the other members a much easier task.

2. *It suggests the probable existence of new elements.* When the periodic law was first formulated there were a number of vacant places in the table which evidently belonged to elements at that time unknown. From their position in the table Mendeléeff predicted with great precision the properties of the elements which he felt sure would one day be discovered to

fill these places. Three of them, scandium, germanium, and gallium, were found within fifteen years, and their properties agreed in a remarkable way with the predictions of Mendeléeff.

3. *It indicates probable errors.* The physical constants of many of the elements did not at first agree with those suggested by the periodic law, and a further study of many such cases showed that errors had been made.

Imperfections of the law. There still remain a good many features which must be regarded as imperfections in the law. Most conspicuous is the fact that the element hydrogen has no place in the table. Moreover, according to their atomic weights, tellurium should follow iodine, argon should follow potassium, and nickel should follow cobalt; but their properties show in each case that this order must be reversed.

The atomic number. The young English physicist Moseley has devised a method of classifying the elements that places them in serial order independently of their atomic weights. The place of each element in this series is called its *atomic number*. In the Moseley system hydrogen comes first, with an atomic number of 1, followed by helium and lithium with atomic numbers of 2 and 3 respectively. These atomic numbers are placed above the symbols of the elements in the periodic table (p. 199). The Moseley system is based on results obtained by X-ray photography, and the elements under this system fall in the same order as their atomic weights save in the case of argon, tellurium, and cobalt. The order of the atomic weights puts these elements in the wrong group; the Moseley system puts them where they belong.

The complex nature of atoms. It was formerly thought that the atoms were indivisible particles; indeed, the word *atom* is derived from Greek words signifying "indivisible." Recent investigations, however, have shown that the atoms are really complex systems which may be likened roughly to miniature solar systems.

CHAPTER XXII

THE CHLORINE FAMILY

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . . .	19.00	-223°	-187°	Pale-yellowish gas
Chlorine (Cl) . . .	35.46	-101.5°	-33.6°	Greenish-yellow gas
Bromine (Br) . . .	79.92	-7.3°	63°	Red liquid
Iodine (I) . . .	126.92	113.5°	184.4°	Purplish-black solid

The family. The four elements named in the above table form a strongly marked family and illustrate very clearly the way in which the members of a family in a periodic group resemble each other, as well as the character of the differences which we may expect to find between the individual members. The elements constituting the family are often termed the *halogens*, a word meaning "producers of salt." Chlorine has already been discussed in Chapter XV. The student should review that chapter in connection with the present one.

FLUORINE

General discussion. It is safe to say that the student of this text has never seen fluorine, and, indeed, very few persons have. This is due to the fact that the element is difficult to prepare and has no uses. Nevertheless its compounds are of considerable importance. Fluorine is a pale-yellowish gas. It is extremely active, even at ordinary temperatures, and is very poisonous. It combines with all the common elements save oxygen. It has a very strong affinity for hydrogen, decomposing water with violence and combining with hydrogen to

form a gas known as hydrogen fluoride (H_2F_2). Of course such an active element would not occur free in nature. Its most important natural compounds are the minerals *fluorite* (CaF_2) and *cryolite* (Na_3AlF_6). Traces of fluorides are also to be found in bones and in the enamel of the teeth.

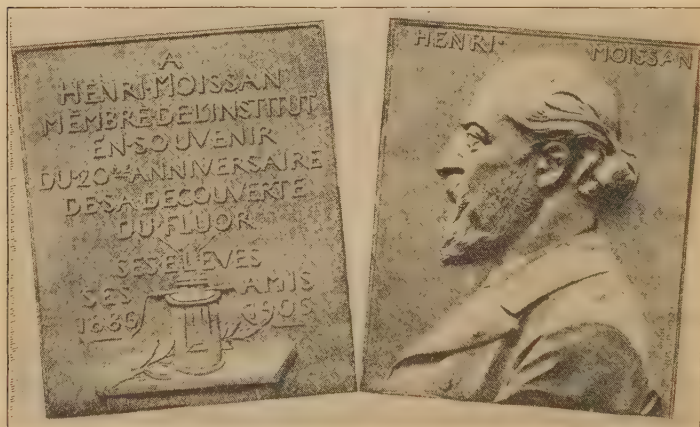


FIG. 112. Tablet erected by the associates and friends of Moissan in his laboratory in Paris in 1906, on the twentieth anniversary of the isolation of fluorine

Preparation. Because of its great activity fluorine is difficult to liberate from its compounds. The French chemist Moissan (Fig. 112) in 1886 finally succeeded in obtaining it in a free state.

Moissan obtained the element by electrolyzing hydrogen fluoride at low temperatures. Pure hydrogen fluoride is a nonconductor; hence Moissan dissolved in it a little potassium acid fluoride (KHF_2) to render it a conductor. A much simpler method of preparation consists in electrolyzing melted potassium acid fluoride (KHF_2). Moissan carried out his experiments in a vessel made of platinum—a metal which is very inactive but very expensive. Copper vessels, however, will do nearly as well and are much cheaper.

Hydrogen fluoride (H_2F_2); hydrofluoric acid. Hydrogen fluoride is a low-boiling liquid (boiling point, 19.4°). It is prepared by the action of sulfuric acid on the mineral fluorite (CaF_2), thus:



It is soluble in all proportions in water, forming *hydrofluoric acid*. This is a strong acid and is extremely corrosive. It readily reacts with sand and powdered quartz, both of which consist of silicon dioxide (SiO_2), to form water and the gas silicon tetrafluoride (SiF_4), thus:



This property makes possible the chief use of hydrofluoric acid; namely, the etching of glass, all varieties of which contain silicon dioxide either free or in combination. The acid is preserved in bottles made of a wax obtained from petroleum and known as *ceresin* (Fig. 113).



FIG. 113. A bottle made out of ceresin for holding hydrofluoric acid

Etching of glass. The glass vessel to be etched is painted over with a protective paint upon which the acid will not act, the parts which it is desired to make opaque being left unprotected. A mixture of fluorite and sulfuric acid is then painted over the vessel, and after a few minutes the vessel is washed clean. Wherever the hydrofluoric acid comes in contact with the glass, it acts upon it, destroying its luster and making it opaque, so that the exposed design will be etched upon the clear glass. Frosted-glass globes are often made in this way, but more frequently by a sand blast. The etching may also be effected by covering the glass with a thin layer of paraffin, cutting the design through the wax, and then exposing the glass to the fumes of the gas.

BROMINE

General discussion. This element, discovered by the French chemist Ballard in 1826, is a dark-red heavy liquid which boils at 63° and freezes at -7.3° . It vaporizes readily at ordinary temperatures. This vapor has an offensive odor and is very irritating to the eyes and throat. One volume of the liquid dissolves in 100 volumes of water. It resembles chlorine in its chemical conduct except that it is less active. Bromine occurs in combination with metals, sodium bromide (NaBr) and magnesium bromide (MgBr_2) being the most abundant forms. These are found in many salt waters. The salt waters obtained by sinking deep wells along the Ohio River and in certain parts of Michigan are the richest in bromine and constitute the source from which the element is prepared.

Preparation. The methods used for preparing chlorine in the laboratory (p. 137) serve also for the preparation of bromine. Commercially it is chiefly prepared by passing an electric

current through salt waters containing bromides. Bromine and some chlorine are liberated; the chlorine, however, assists in the reaction, since it decomposes the unchanged bromides, liberating bromine, thus:

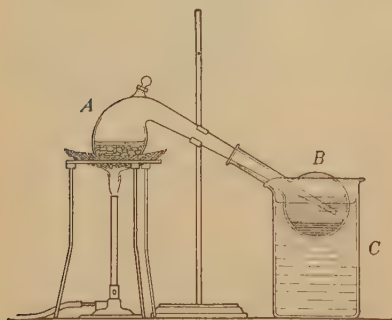
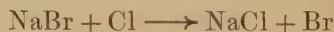
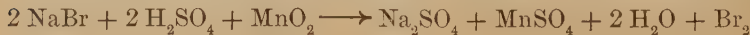


FIG. 114. An apparatus for the preparation of bromine in the laboratory

Laboratory preparation of bromine. A mixture of sodium bromide and manganese diox-

ide is introduced into the retort *A* (Fig. 114). Sulfuric acid is added and the mixture heated. Bromine is liberated and condenses in the flask *B*, kept cool by ice water in the beaker *C*. The equation is



Hydrogen bromide (HBr); hydrobromic acid. Hydrogen bromide is a colorless gas resembling hydrogen fluoride and hydrogen chloride except that it is less stable (that is, more easily decomposed). Its solution in water constitutes *hydrobromic acid*. The salts of hydrobromic acid are known as *bromides*. They resemble the chlorides in their properties.

Uses. Bromine is used in making certain dyes and medicines and in the preparation of bromides. Silver bromide (AgBr) is used extensively in photography, while sodium bromide and potassium bromide are common drugs.

Bromine in the World War. Among the poison gases used in the World War were certain compounds known as *lachrymators* because they caused inflammation of the eyes and a copious flow of tears. Bromine is the essential constituent of the most effective of these lachrymators. To obtain supplies of bromine necessary for their production the United States, during the war, sunk sixteen wells in the vicinity of Midland, Michigan. These wells represent a total possible output of bromine amounting to about 500,000 pounds annually.

IODINE

General discussion. Iodine was discovered in the ashes of sea plants by the French chemist Courtois in 1812. It differs from the other halogens in that it is a purplish-black, shining crystalline solid. When warmed it gives off a beautiful violet vapor. It is only very slightly soluble in water, but readily dissolves in carbon tetrachloride and in alcohol. It resembles chlorine in its chemical conduct, but is even less active than bromine. Even a very small amount of free iodine colors starch blue — a reaction which is used to detect the presence of both iodine and starch. Small amounts of iodine are found combined with metals in sea water, from which it is absorbed by certain sea plants, so that it is found in their ashes. It is also found in Chile as a constituent of sodium nitrate (Chile saltpeter).

Preparation. In the laboratory iodine is prepared in the same way as bromine, using NaI in place of NaBr (p. 206). Commercially iodine was formerly obtained entirely from the ashes of seaweed (*kelp*), and a limited quantity is still obtained from this source. Most of our supply comes from the beds of Chile saltpeter.

Hydrogen iodide (HI); hydriodic acid. Hydrogen iodide is a colorless gas, but is less stable than the corresponding compounds of the other halogens. Its solution in water constitutes *hydriodic acid*. The salts of this acid are called *iodides*, and these in general resemble the chlorides and bromides.

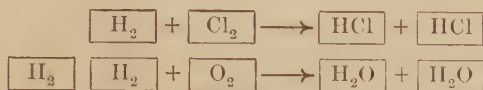
Use. A solution of iodine in alcohol is known as *tincture of iodine* and constitutes one of our most common antiseptics. Potassium iodide (KI) is used in medicine, and iodine has many uses in chemical analysis.

Properties of the halogens contrasted. By studying the table at the head of this chapter it will be noted that the halogens exhibit a regular gradation of properties. Fluorine is a light, slightly colored gas, chlorine is a heavier gas with more marked color, while bromine is a red liquid, and iodine a nearly black solid. Their melting points and boiling points *increase with their atomic weights* (see table). Their affinity for hydrogen and the metals, on the other hand, *decreases with their atomic weights*, that of fluorine being the greatest and iodine the least. Fluorine and bromine do not combine with oxygen, while chlorine and iodine form unstable oxides.

GAY-LUSSAC'S LAW OF VOLUMES

Experiments show that *1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride*. Similar combining ratios hold good when hydrogen combines with the vapor of bromine and of iodine. These facts recall the simple volume relations already noted in the study of the composition of

steam (p. 71). These relations may be represented graphically in the following way, the squares representing *equal volumes*:



In the early part of the past century the distinguished French chemist Gay-Lussac (Fig. 26) studied the volume relations of many combining gases and concluded that similar relations *always* hold. His observations are summed up in the following generalization, known as the law of volumes: *When two gases combine chemically there is always a simple ratio between the volumes that combine and also between the volume of either one of them and that of the product, provided it is a gas.* By a simple ratio is meant, of course, the ratio of integer numbers; as, 1 : 2 or 2 : 3.

EXERCISES

1. Give the name and the nationality of the discoverer of each of the halogens.
2. Contrast the properties of the halogens.
3. Contrast the chemical conduct of the halogens.
4. (a) Give the names and formulas of the compounds that each of the halogens forms with hydrogen. (b) To what class of compounds do they belong?
5. What elements are liquids at ordinary temperature?
6. Consult the dictionary for the significance of the names of each of the halogens.
7. (a) How do you account for the fact that the pure liquid hydrogen fluoride is a nonconductor of electricity? (b) How did Moissan render it a conductor?
8. In what other connection has the name of Moissan been mentioned?
9. Why cannot fluorine be prepared by electrolyzing hydrofluoric acid?

10. Why do we write the formula for hydrogen fluoride as H_2F_2 while that for hydrogen chloride is written HCl ?

11. (a) What gas has been studied that resembles the vapor of bromine in color? (b) How could you distinguish between the two?

12. Why do solutions of hydrogen bromide and hydrogen iodide color on standing, while hydrogen fluoride and hydrogen chloride do not?

13. Sodium chloride, sodium bromide, and sodium iodide are all white crystalline solids. How could you distinguish between them?

14. What reaction would take place if chlorine were passed into a solution (a) of sodium bromide? (b) of sodium iodide?

15. Suppose that iodine were added to a solution of sodium chloride. Would any reaction take place?

16. Enumerate the acids so far studied, giving the composition of each.

17. Two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapor (see Gay-Lussac's law of volumes, p. 209). Show that this fact is in accord with Avogadro's principle (p. 47).

18. A certain mineral is known to be either rock salt (NaCl) or fluorite. How could you decide which it is?

19. What weight of fluorite is necessary for preparing 100 g. of hydrofluoric acid containing 50 per cent of hydrogen fluoride?

20. The salt water used in preparing bromine contains 0.12 per cent of bromine; 1 ton of this brine would yield how many pounds of bromine?

21. What weight of sodium iodide would be required for the preparation of 10 g. of iodine?

CHAPTER XXIII

HYDROCARBONS ; PETROLEUM

Hydrocarbons. Carbon and hydrogen unite to form a great many compounds, and these are known as the *hydrocarbons*. Their importance may be inferred from the fact that, mixed together in varying proportions, they constitute such valuable substances as *natural gas*, *gasoline*, *kerosene*, *lubricating oils*, *vaseline*, and *paraffin*.

In order to simplify the study of the hydrocarbons it is convenient to arrange them in groups, or *series*. The most extensive of these is the *methane* series. In the following table are given the names, formulas, and boiling points of some of the members of this series :

	BOILING POINT		BOILING POINT
Methane (CH_4) . . .	-160°	Pentane (C_5H_{12}) . . .	$+36^\circ$
Ethane (C_2H_6) . . .	-93°	Hexane (C_6H_{14}) . . .	$+69^\circ$
Propane (C_3H_8) . . .	-45°	Heptane (C_7H_{16}) . . .	$+98^\circ$
Butane (C_4H_{10}) . . .	$+1^\circ$	Octane (C_8H_{18}) . . .	$+125.5^\circ$
General formula ($\text{C}_n\text{H}_{2n+2}$)			

It will be noted that each member of this series differs from the one preceding it by the group of atoms CH_2 , and that the boiling points gradually increase. All the members of this series are known up to the one having the formula $\text{C}_{28}\text{H}_{58}$. The lower members are colorless gases, the intermediate members are liquids, and the higher members are solids. They are insoluble in water and are all combustible, the carbon present burning to carbon dioxide and the hydrogen to water.

Petroleum and products derived from it. Petroleum is a dark-colored liquid found in the earth in certain localities. This liquid is composed principally of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons. Crude petroleum is not only used as fuel in this country, particularly on locomotives and ships, but many useful products are obtained from it by the process of *refining*, among them *gasoline*, *kerosene*, *lubricating oils*, *vaseline*, and *paraffin* (Fig. 117). These products are not single compounds, but are mixtures of compounds boiling between certain limits. When pure they are all colorless. Sometimes the commercial products are colored by impurities.

The refining of petroleum. In this process the crude oil is run into large iron stills (Fig. 116) and is then distilled. The distillates which pass over between certain limits of temperature are kept separate and, after being purified by treatment with sulfuric acid and then with sodium hydroxide and water, serve for different uses. The liquid passing over between approximately 70° and 150° is known as *naphtha*, while that passing over between 150° and 300° constitutes ordinary *kerosene*. A number of different naphthas are recognized commercially, differing in boiling points and density. Those of low boiling-point constitute ordinary *gasoline* and are used as a fuel in stoves and motors; those of higher boiling-points are used in making paints. *Benzine* is a low-boiling naphtha and, being a good solvent for such organic substances as fats and oils, is used in cleaning fabrics (dry-cleaning).

The liquid remaining after the kerosene and higher-boiling oils have distilled over is chilled, whereupon the solid constituents dissolved in the oil separate. These are filtered off and constitute ordinary *paraffin*. The filtrate is then distilled, and from it various *lubricating oils* are obtained.

Formerly kerosene was the most important of the products obtained from petroleum. At present, however, gasoline is the most in demand, so that every effort is made to increase the yield. To accomplish this efficiently the distillation is carried on under conditions that tend to decompose the heavier molecules

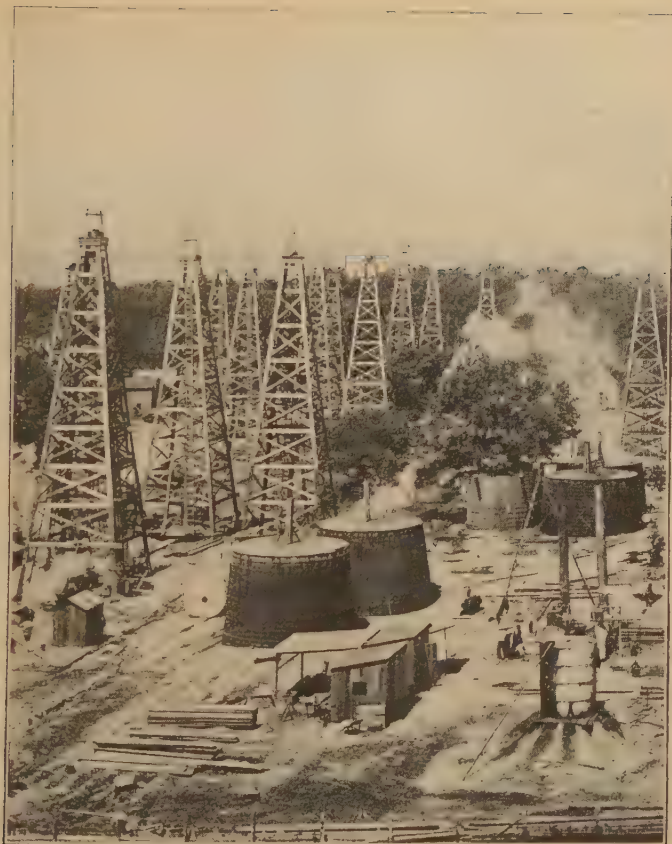


FIG. 115. Typical scene in an oil field

Wells are sunk into the oil-bearing strata, which vary in depth from a few feet to 4000 feet or more. Sometimes the oil in the strata is under such pressure that it will flow from the well in large volumes under its own pressure; more often the oil must be pumped to the earth's surface. This crude oil, commonly called *petroleum*, is stored in tanks (see figure) until it is desired to refine it. In the United States the chief oil-producing regions at present are Texas, California, Oklahoma, and Pennsylvania. The total production varies from year to year, but is gradually increasing with the greater demand for gasoline and other products obtained from the oil. At present between 4,000,000 and 5,000,000 barrels of petroleum are produced annually, while the annual gasoline production amounts to nearly 4,000,000,000 gallons

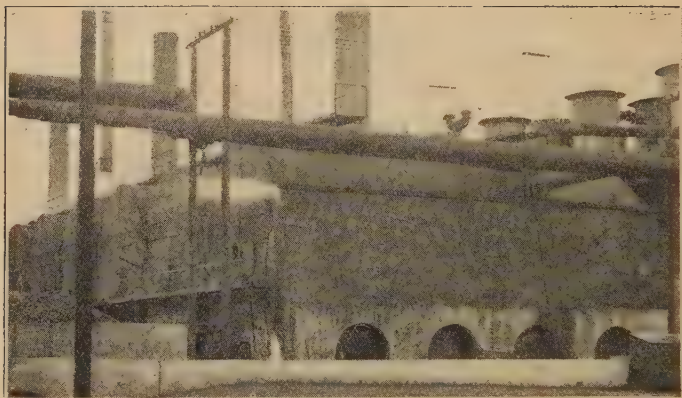


FIG. 116. View of stills for refining petroleum

Sometimes the petroleum is used directly as a fuel. More often it is *refined*. This process consists in separating it into different constituents by distillation and purifying these products chiefly by washing them first with sulfuric acid, then with sodium hydroxide, and finally with water. The distillation is carried on in large iron stills, shown in the figure



FIG. 117. Crude oil and the chief products obtained from it

making up the higher-boiling liquids into the simpler molecules which constitute liquids of lower boiling-points. The process is known as the *cracking* of oils.

Use of benzine and gasoline in our homes. Because of the ease with which benzine and gasoline (these two terms are often used interchangeably) burn, and also because of the explosive character of their vapor when mixed with air, accidents often result from their use, especially when they are employed in our homes for cleaning fabrics. Recent statistics show that in a single year 1040 persons were burned to death and 3120 injured as a result of gasoline fires. It is obvious, therefore, that the greatest care should be exercised in its use.

Fractional distillation. The process of purifying a mixture such as petroleum is known as *fractional distillation*. In this process the mixture is heated, and in a general way the compounds distill over in the order of their boiling points. By repeating the process it is ordinarily possible to separate a mixture into the compounds present. In the refining of petroleum it is not necessary to effect such a sharp separation, but only to obtain a mixture of compounds which boil within certain limits.

Asphalt. When petroleum from certain sources is distilled there is left in the retort a heavy, tarry liquid. A similar substance is found in nature, both in the liquid and the solid form, and is known as *asphalt*. The most important deposit of asphalt is on the island of Trinidad (Fig. 118). Asphalt is used for road construction, for making paints, and for roofing.

Methane (CH₄). Pure methane is a colorless, odorless gas about one half as heavy as air. It is commonly known as *marsh gas*, since it is formed in marshes and, in general, wherever organic matter decays or is heated in the absence of air. It constitutes about 30 per cent of coal gas and from 90 per cent to 95 per cent of natural gas. It often collects in mines, and when mixed with air is called *fire damp*. Such mixtures are very explosive. When ignited it burns with a pale-blue flame:



Safety lamp. Fortunately the ignition point of fire damp (that is, the temperature at which it takes fire) is high and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (Fig. 86) invented a miner's lamp based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 119). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases and the explosion is confined to the



FIG. 118. Mining asphalt on Trinidad island for use in road construction

interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen flame and parallel with the table (Fig. 120). When the gas is turned on and a light applied above the gauze, the resulting flame rests upon the gauze, but does not pass through it to the burner.

Halogen derivatives of methane. As a rule the hydrogen present in a hydrocarbon may be displaced by a halogen element, atom for atom. In this way there are formed from methane a number of derivatives, the most important of which are the following:

Chloroform (CHCl_3), a heavy, colorless liquid boiling at 61° , is the well-known anæsthetic used in surgery. *Carbon tetrachloride*

(CCl_4) resembles chloroform in appearance. It is a good solvent, especially for fatty substances. It is often used to remove grease spots from fabrics and is sold for this purpose under the name of *carbona*. It possesses the advantage over benzine of being noninflammable, but it is more expensive. Large quantities are used as a fire extinguisher (*pyrene*) (p. 114). *Iodoform* (CHI_3) is a yellow crystalline solid and is largely used as an antiseptic in the treatment of wounds.

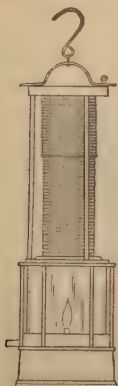
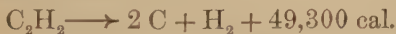


FIG. 119. The miner's safety lamp

Acetylene (C_2H_2). In addition to the hydrocarbons composing the methane series, many others are known. Among these is *acetylene*. This is a colorless gas having, when pure, a faint, pleasant odor. It is easily obtained by the action of water on calcium carbide (CaC_2):



In this way the gas is prepared in large quantities for use as an illuminant and as a source of intense heat. When heated it decomposes, with evolution of a great deal of heat:



By this method the Germans prepared much of the hydrogen used for filling the Zeppelins in the World War.

When compressed in cylinders acetylene is very explosive, since the heat liberated in compressing the gas is sufficient to start decomposition. With the proper admixture of air it burns with a brilliant white light. The flame is very hot, because to the heat of combustion of the hydrogen and the carbon there is added the heat of decomposition of the acetylene undergoing combustion:

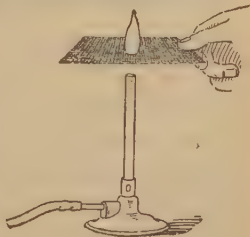
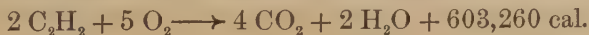


FIG. 120. An experiment to illustrate the principle of the safety lamp

Uses of acetylene. Acetylene is chiefly used as an illuminant when electric lights are not available. It may be safely stored in metal cylinders by filling the cylinder with some porous material (such as asbestos and cotton), partially saturating this with a liquid compound called *acetone*, and then



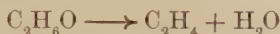
FIG. 121. Cutting an iron plate by means of the oxyacetylene blowpipe

forcing in the gas at low temperatures. Under pressure the acetone dissolves a large volume of the gas. In this form it is now a common article of commerce.

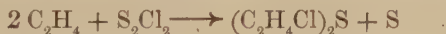
The intense heat generated by the combustion of acetylene makes it useful in certain processes requiring high temperatures, such as burning the carbon out of motor engines and the welding and cutting of metals. For this purpose the acetylene is burned in an apparatus known as the *oxyacetylene blowpipe*, which is very much like the blast lamp in principle. A temperature of about 2700° may be obtained in this way. This blowpipe has been found especially useful in cutting iron structures (Fig. 121), since the tip of the flame, when drawn

slowly over the metal, melts and burns it at the point of contact and thus makes it possible to cut the metal into pieces.

Ethylene (C_2H_4). Small percentages of this gas are present in coal gas. It is prepared by heating the vapor of ordinary alcohol (C_2H_6O) in contact with kaolin (a compound of aluminium), which acts as a catalytic agent:



During the World War the United States prepared enormous quantities of ethylene for use in the manufacture of the poison liquid known as *mustard gas*. This compound, while called a gas during the war, is really a high-boiling, nearly colorless liquid. It has the formula $(C_2H_4Cl)_2S$, and its chemical name is *dichloroethyl sulfide*. It is absorbed by the skin, and after absorption it decomposes, forming hydrogen chloride, which produces large blisters and causes severe and often fatal inflammation. The compound is made according to the following equation:



EXERCISES

1. Can the flame of gasoline be extinguished by water?
2. How could you distinguish between gasoline and kerosene?
3. Why not burn gasoline in lamps?
4. Why not substitute coal oil for gasoline in motor-car engines?
5. Distinguish between fractional distillation and destructive distillation.
6. Methane is formed when organic matter decays under water. (a) Might this account for the formation of natural gas? (b) What is the function of the water?
7. How do you account for the formation of carbon monoxide in a gasoline engine (p. 114)?
8. It is stated that in the gasoline engine, as ordinarily operated, about 30 per cent of the effective power of the gasoline is not recovered. Suggest a reason for this.
9. Under what conditions is natural gas explosive?
10. Write the equations for the combustion of methane; of acetylene.

11. In what proportions by volume ought acetylene and oxygen to be mixed in an oxyacetylene blowpipe to get the maximum heat?

12. In a general way, to what extent is modern civilization dependent on petroleum?

13. What products of petroleum are used in your home?

14. Under what conditions would natural gas become a liquid?

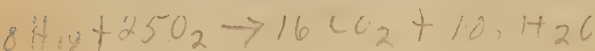
15. Kerosene is a good solvent for fats and oils. Why not use it in place of gasoline for cleaning fabrics?

16. Why is it that kerosene is so much safer to handle than gasoline?

17. Suppose you were given two bottles, the one filled with hydrogen and the other with marsh gas, how would you proceed to determine which of the two contained the hydrogen?

18. Assuming that natural gas is pure methane, (a) what volume of oxygen would be required for the combustion of 1000 cu. ft. of the gas? (b) what volume of carbon dioxide would be produced? (Solve by inspection of equation, p. 115.)

19. (a) Write the equation for the combustion of octane. (b) Assuming that gasoline is pure octane and that 1 gallon of it weighs 3500 g., what weight of oxygen would be required for the complete combustion of 1 gallon of gasoline? (c) What volume of air would be required to furnish this amount of oxygen?



CHAPTER XXIV

FUELS; ELECTRIC FURNACES; FLAMES

Fuels. A variety of substances are used as sources of heat, the most important of them being the various fuel gases, together with coal, wood, and petroleum. The composition of a number of these fuel gases is given in the table on page 224. Most of them serve as illuminants as well as fuels.

Coal gas. It has been known for several centuries that when soft (bituminous) coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was used for street lighting in London and Paris more than a hundred years ago.

Manufacture of coal gas. The manufacture of coal gas is represented in a diagrammatic way in Fig. 122. The coal is introduced into a closed retort *A* and heated by the fire below. A number of these retorts are placed in parallel rows, each being furnished with a delivery pipe. These pipes lead into a large pipe *B* (known as the *hydraulic main*), which runs at right angles to the retorts. When the coal is heated out of contact with air a large number of compounds are formed, some of which, at ordinary temperatures, are gases, others are liquids, and others are solids. These escape into the hydraulic main, and, the temperature being reduced somewhat, some of the products that are liquid or solid at ordinary temperature condense in the form of a black, tarry mass known as *coal tar* and are continuously drawn off. The gas then passes into the cooler *C*, where the remaining tar condenses. On the top of the tar there collects a liquid containing ammonia and known as *ammoniacal liquor* (p. 164). In the scrubber *D* the partially purified gas passes through a column of loose coke, over which water is sprayed, where it is still further cooled and to

some extent purified from soluble gases such as hydrogen sulfide and ammonia. In the purifier *E* it passes over a bed of lime or of iron oxide, which removes the remainder of the sulfur compounds, and from this it enters the large gas holder *F*, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal,

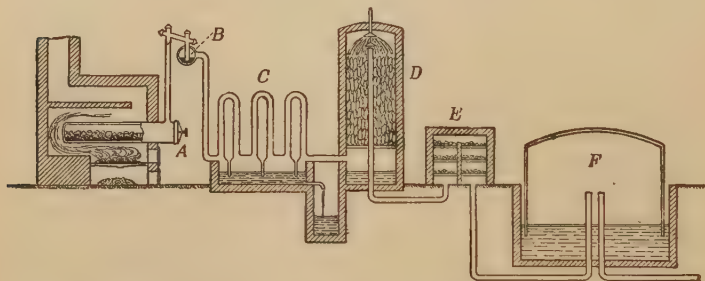


FIG. 122. Diagram of a plant used for the manufacture of coal gas and its by-products. In some plants the retort *A* is placed in an upright position

the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor.

Not only is the ammonia obtained in the manufacture of the gas of great importance, but the coal tar is the source of many very useful substances, as will be explained later.

The by-product coke oven. It will be observed that coke is formed in the process used in the manufacture of coal gas. Coke is a very important product and is used in large quantities, especially in the reduction of metals, such as iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. Much of the additional coke required has been prepared by coking the coal in ovens called *beehive ovens* because of their shape. The coking of coal in these ovens is carried out as follows: The oven is nearly filled with coal, and the coal is ignited. After the fire is well started the draft is shut off, and the heat formed in the combustion of a portion of

the coal is sufficient to coke the remainder of the coal. In this process all the coal tar, coal gas, and ammonia escape through an opening in the top of the furnace and are lost.

The growing demand for ammonia, as well as for the products obtained from coal tar, has led to the construction of furnaces or ovens for the coking of coal which make it possible to save the coal tar and ammonia formed in the process. Such ovens are

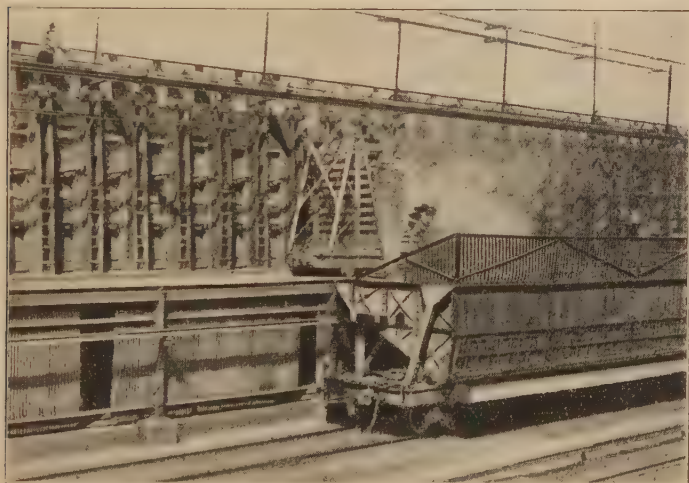


FIG. 123. View of a by-product coking plant

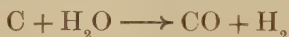
The coal is heated in the narrow ovens. The view shows the coke being removed from one of the ovens

known as *by-product coke ovens*, this term being chosen because the ammonia and coal tar formed in the process of coking the coal are by-products, the coke being the main product. Even at present more coke is made in the by-product ovens than in the beehive, and the percentage will undoubtedly increase since we cannot afford to waste such valuable products as are wasted in the beehive ovens.

• Fig. 123 represents a portion of a large by-product coking plant. It consists primarily of a number of narrow, upright ovens placed side by side, but separated sufficiently to admit of heating the coal

with which the ovens are filled. As a rule a portion of the gas generated in the process is used as a fuel for coking the coal. The hot flame of the burning gas strikes against the bottom and sides of the ovens. The coal tar and ammonia are separated and collected as in the manufacture of coal gas; indeed, the by-product oven is a large coal-gas plant. When the process is complete each oven is pushed forward and the coke dropped into a car, as shown in the figure.

Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is made by passing steam over very hot anthracite coal or coke, when the reaction shown in the following equation takes place:



The coal is burned in a draft of air until it is very hot. The air is then shut off and steam turned on. The temperature gradually falls because the reaction absorbs heat, and when it reaches about 1000° the steam is cut off and the air supply renewed.

Water gas is very effective as a fuel, since both carbon monoxide and hydrogen burn with very hot flames. It has little odor and is very poisonous. Its use is therefore attended with some risk, since leaks in pipes are very likely to escape notice.

Enriched water gas. When required merely for the production of heat, the gas as prepared above is at once ready for use. When made for illuminating purposes it must be *enriched*; that is, illuminants must be added, since both carbon monoxide and hydrogen burn with a nonluminous flame. This is accomplished by passing it into heaters containing highly heated petroleum oils. The gas takes up the gaseous hydrocarbons formed in the decomposition of the petroleum oils, and these hydrocarbons make it burn with a luminous flame.

Producer gas. Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal under such conditions

that the product of combustion is largely carbon monoxide (Fig. 124). Very often a little steam is admitted with the air, and this on passing through the hot bed of coals is reduced as in the preparation of water gas. Made in this way, producer gas is composed mainly of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality, even from lignite, and as gas engines run well with this gas, it furnishes the most economical method for utilizing low-grade coal for power.

Natural gas. In many regions of the United States, as well as in other countries, natural gas is obtained from wells drilled into a rock stratum holding the gas. While it is

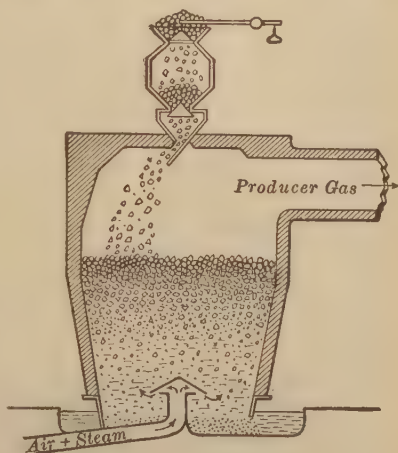


FIG. 124. Diagram of the method of making producer gas

variable in composition, it consists largely of methane, many samples containing as much as 95 per cent of this compound. It burns with a rather smoky flame of moderate luminosity, but works well with a gas mantle. It has a high heat of combustion, as shown in the following equation:



It is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities.

Comparative composition of fuel gases. The figures in the table on page 224 are the results of analyses of average samples, but since each kind of fuel gas varies considerably in composition, the values are to be taken as approximate only.

COMPOSITION OF GASES

CONSTITUENT	OHIO NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
H ₂	0.9	41.3	52.88	37.96	10.90
CH ₄	89.5	43.6	2.16	7.09	
C ₆ H ₆	9.3			2.01	
C ₂ H ₂ and C ₂ H ₄ . . .	0.3	3.9		9.40	0.60
CO	0.4	6.4	36.80	32.25	20.10
CO ₂	0.3	2.0	3.47	4.73	8.50
N ₂	0.2	1.2	4.69	3.96	59.90
O ₂	0.0	0.3		0.60	
Other hydrocarbons . .	0.0	1.5		1.80	

Products of the combustion of ordinary fuels. Ordinary fuels, such as oil, wood, coal, and fuel gases, are largely made up of carbon and hydrogen or their compounds. The chief products of the combustion of such fuels are carbon dioxide and water. Associated with these are small amounts of other products, such as carbon monoxide and sulfur dioxide, the latter being formed from traces of sulfur compounds in the fuels.



FIG. 125. Determining the calorific value of coal in the laboratory of the American Rolling Mill Company

Rooms are not infrequently heated by gas or oil stoves, with no provision for removing the products of combustion. Likewise, natural gas is often burned in stoves or grates with the damper closed so as to leave no opening into

the chimney. Such practices are greatly to be condemned, since the air in the rooms heated in this way soon becomes saturated with water vapor and so contaminated with the other products of combustion as to render it unfit for respiration. In walking along a street in cold weather one can pick out the rooms that are heated in this way, for the windows of such rooms are covered with a film of moisture.

Calorific value of fuels.

The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. *The heat evolved by the combustion of one gram of a fuel is called its calorific value.* In large contracts the price paid for a fuel is generally based on its calorific value, as well as upon its adaptability

to the use to which it is to be put. The calorific value of (say) coal is determined by burning a definite weight of the sample in a bomb calorimeter constructed on the principle shown in Fig. 37, but fitted with a top so that it can be kept closed during the combustion (Fig. 126). The table on page 226 will give some average values for a few common fuels:

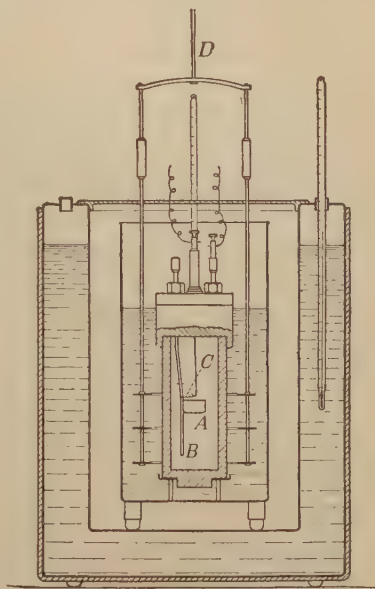


FIG. 126. A bomb calorimeter for determining the calorific value of coal

The coal is placed in the capsule *C*. The calorimeter is then filled with oxygen under pressure and the coal ignited by an electric current. After the coal is burned, the increase in the temperature of the water is noted and the calorific value deduced from this

CALORIFIC VALUE OF FUELS

Wood (air-dried)	about 3800-4000 cal.
Bituminous coal (Pennsylvania), 35 % volatile matter, 6 % ash	about 8300 cal.
Bituminous coal (Pocahontas), 18 % volatile matter, 6 % ash	about 8700 cal.
Anthracite coal, 12 % ash	about 7300 cal.
Coke, 10 % ash	about 7300 cal.

The electric furnace. In recent years electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can easily be reached. These furnaces are constructed on one of two general principles.



FIG. 127. An arc furnace

1. **Arc furnaces.** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 127. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc.

2. **Resistance furnaces.** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. A typical form of such a furnace is illustrated in Fig. 60, which is used in the manufacture of graphite.

Conditions necessary for flames. When one of the substances undergoing combustion remains solid at the temperature occasioned by the combustion, light may be given off, but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, but no flame is seen. When, however, both of the substances involved are gases or vapors at the temperature reached in the combustion, the act of union is accompanied by a *flame*.

Flames from burning liquids or solids. Many substances which are liquids or solids at ordinary temperatures burn with a flame because the heat of combustion slowly vaporizes them, and the

flame is due to the union of this vapor with the oxygen of the air. This may be shown in the case of a candle flame by holding one end of a slender glass tube in the base of the flame (Fig. 129). The unburned vapor in the inner part of the flame is thus conducted away and may be ignited at the upper end of the tube.

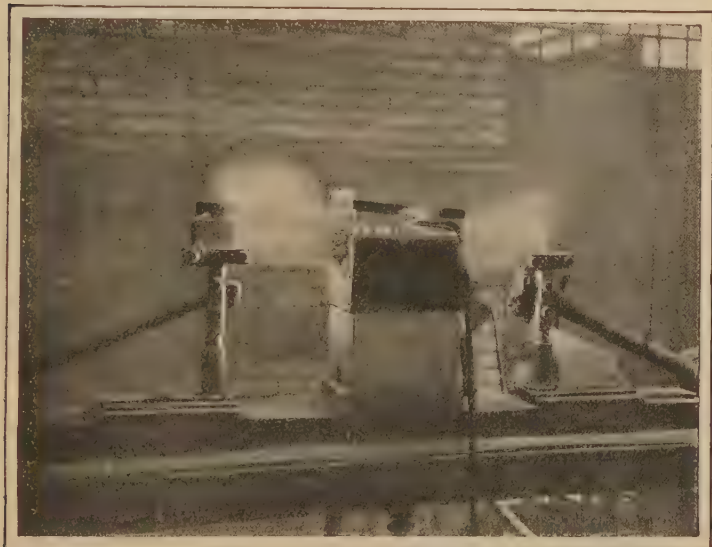


FIG. 128. View of an electric furnace used by Moissan, who was one of the first scientists to experiment with reactions at high temperatures

From Duncan's "Chemistry of Commerce"

Structure of a flame. When hydrogen or carbon monoxide burns in oxygen, but one reaction takes place, and as a result the flame is very simple in structure. It consists of a colorless inner cone of unburned gas and an outer cone in which the union between the hydrogen and the oxygen is taking place. It follows that the outer cone is the hot part of the flame. That the inner cone is cool is shown by the fact that a match head suspended in this region (Fig. 130) before lighting the gas, and left there while the gas burns, is not ignited.

The flames produced by the combustion of hydrocarbons such as are present in coal gas and natural gas or of mixtures of hydrocarbons with stearic acid, as in candles, is much more

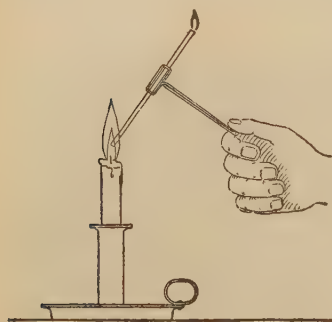


FIG. 129. Method of proving that the interior of a candle flame contains combustible vapors

complex because several consecutive reactions take place. For example, in the candle flame (Fig. 131) there are, broadly speaking, three cones: (1) the inner cone *A*, composed of combustible vapors; (2) an intermediate cone *B*, in which these vapors are decomposed by the heat and a small quantity of carbon is set free which renders the flame

luminous; and (3) an almost invisible, narrow outer cone, or film, *C*, in which the hydrogen and carbon are burned to water and carbon dioxide respectively.

Bunsen burners. In the ordinary Bunsen burner used in chemical laboratories, and in similar burners used in gas stoves and ranges (Fig. 132) and for illumination with the aid of mantles, the gas is mixed with a certain percentage of air before it is burned. This is accomplished by having an opening (mixer) in the base of the burner (Fig. 132, *A*) into which the air is drawn by the flow of the gas. If the mixer is adjusted properly so that just the right amount of air is admitted, the flame is colorless. Such a flame possesses an advantage in that no carbon is deposited from it.

complex because several consecutive reactions take place. For example, in the candle flame (Fig. 131) there are, broadly speaking, three cones: (1) the inner cone *A*, composed of combustible vapors; (2) an intermediate cone *B*, in which these vapors are decomposed by the heat and a small quantity of carbon is set free which renders the flame



FIG. 130. A match head suspended in lower part of gas flame is not ignited

Smoke prevention. Since the products of combustion of fuels are carbon dioxide and water vapor, and these are invisible compounds, it is evident that if the combustion is complete



FIG. 131. The cones of a candle flame

no smoke will be formed. As a rule the combustion is imperfect; gaseous compounds containing carbon are first formed, and when these are imperfectly burned, a part of their carbon is set free in a finely divided state constituting *smoke*. Smoke may therefore be prevented by securing the complete combustion of the fuel, the necessary conditions being as follows: (1) a sufficient supply of air; (2) thorough mixing of the air with the combustible gases produced from the fuel; and (3) a temperature high enough to maintain active combustion.

Smoke prevention is a problem of great economic importance, especially in the large cities. Thus, for example, it has been estimated that the smoke in the city of Pittsburgh costs the people of the city \$10,000,000 yearly, or about \$20 for each inhabitant; and this does not take into account the serious effect of smoke upon health. Because of these facts many cities are now taking steps to abate the smoke nuisance. This is done by compelling the use of furnaces so constructed as to secure the conditions (noted above) for complete combustion.

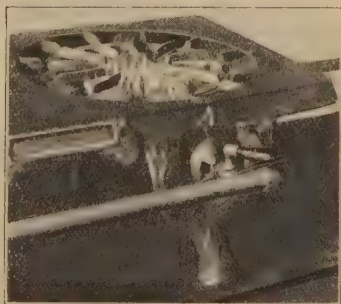


FIG. 132. A typical gas burner

Gas mantles. In using the fuel gases as illuminants the gas is generally mixed with air before burning. In this way the gas burns with a hot but nearly nonluminous flame. The light is obtained by suspending about this flame a gauze mantle of suitable

material. The successful development of the gas mantle was a great chemical achievement, for very few materials are suited to the purpose, and these are very rare in nature and difficult to purify. The best mantles are composed of a mixture of 99 per cent of thorium oxide with 1 per cent of cerium oxide.

The thorium and cerium compounds used in gas mantles are obtained from *monazite sand* (Fig. 133), found principally in Brazil. The process of making a gas mantle consists in knitting a cylindrical cotton fabric, which is then dipped into a solution of the nitrates

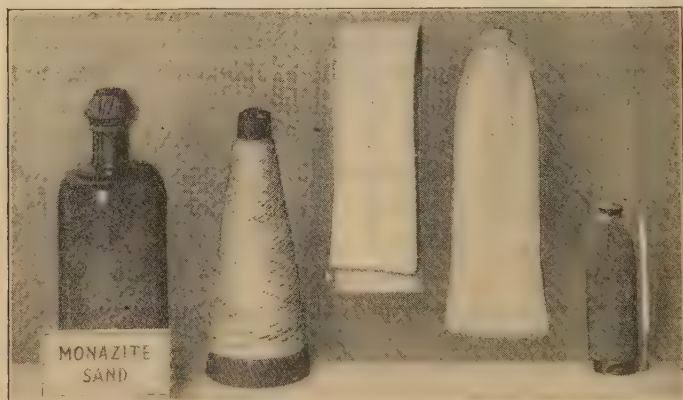


FIG. 133. Materials used in making gas mantles; also different stages in the process

of thorium and cerium. After drying, the fabric is heated, in which process the yarn is burned, while the nitrates of thorium and cerium are converted into oxides which are left in the form of the original fabric. The resulting mantle is very delicate and is strengthened for shipping by dipping it into a solution of an appropriate substance and drying.

EXERCISES

1. Enumerate some important substances obtained in the destructive distillation of wood; of coal.
2. Why not use hard coal in preparing coal gas?
3. How do you account for the presence of nitrogen (*a*) in water gas (see table, p. 224)? (*b*) in producer gas?

4. (a) Why do the windows of rooms heated by portable gas stoves *sweat* in cold weather? (b) Is the moisture on such windows on the inside or the outside of the glass?

5. Why do some samples of charcoal burn with a flame while others do not?

6. What rare element is found in the natural gas of certain localities?

7. What is the disadvantage of water gas as an illuminant?

8. Which of the gases whose composition is given in the table (p. 224) should you expect to have the least heat value?

9. Venders of some forms of gas stoves often claim that no products are evolved when gas is burned in their stoves because the gas is completely consumed. Is this contention correct?

10. Why is carbon deposited on cooking vessels heated over a flame?

11. A candle (composed of compounds of carbon and hydrogen) is burned in a closed volume of air. State the changes that take place both in the candle and in the air.

12. Why does bituminous coal burn with more of a flame than anthracite?

13. 1000 cu. ft. of methane weighs about 20.3 kg. Assuming natural gas to be pure methane, what is the heat evolved in the combustion of 1000 cu. ft. of the gas?

14. The fuel value of a coal was determined by burning 1 g. of the coal in a calorimeter containing 2500 g. of water. The heat liberated raised the temperature of the water 3.1° . Calculate the calorific value of the coal. $2500 \times 3.1 = 7750$

15. A portable gas stove used in heating a room burns 10 cu. ft. of gas each hour. If the gas is pure methane, (a) what volume of oxygen is withdrawn each hour from the air in the room? (b) what volume of carbon dioxide is evolved? $24 + 2$

CHAPTER XXV

COAL-TAR COMPOUNDS

General discussion. We have seen that in the manufacture of coke and coal gas there is obtained a tarry mass known as *coal tar*. This is an exceedingly complex mixture of various compounds colored black with finely divided carbon.

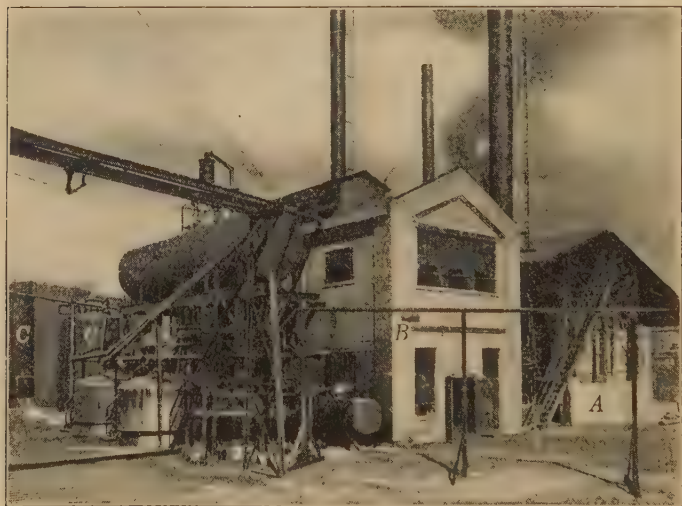


FIG. 134. View of a modern plant for distilling coal tar

When coal gas was first prepared, this tarry mass was regarded as a nuisance, and it was a source of expense to dispose of it. Later, chemists began to find in it some useful compounds, and this investigation has gone on until now coal tar is of inestimable value, furnishing us with thousands of compounds of the greatest importance to our welfare.

This achievement shows something of the part that the chemist is taking in the advancement of modern civilization.

Useful products are obtained from coal tar by much the same methods as are used in refining petroleum. The tar is subjected to fractional distillation, and the various products which are separated in this way are then further purified.

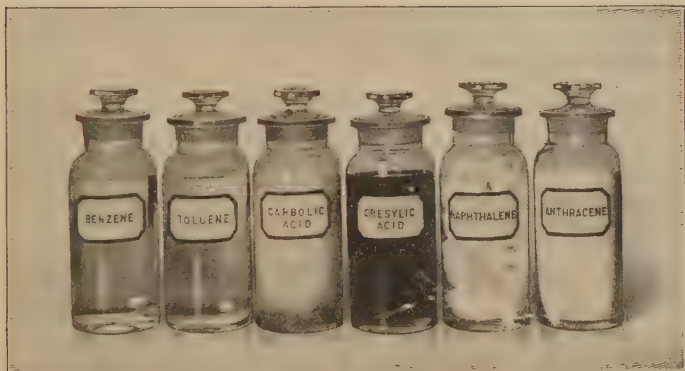


FIG. 135. Some of the principal constituents obtained directly from coal tar

Fig. 134 shows a modern plant for distilling coal tar. The large stills in which the coal tar is distilled are shown in the shed *A*, the vapors obtained on heating the tar are passed through condensers (housed in *B*), and the resulting products are stored in containers, two of which, *C*, *C*, are shown in the figure.

Coal-tar compounds. While there are many compounds in coal tar, it has been found economical to separate from it only eight or ten of them. The six most important of these are shown in Fig. 135. Each of these compounds, however, serves as the *source material* for the preparation of other compounds and these in turn for still others. *All these compounds, whether present in coal tar or prepared from those that are present in coal tar, are known collectively as coal-tar compounds.* Many thousands of them are known.

The chart (Fig. 136) gives us some idea of the kind of compounds that are derived from coal tar and also the relation of the compounds to each other. Thus, *toluene* is obtained directly from coal tar, as indicated by the arrow, while from toluene (following the arrows) we obtain benzoic acid, trinitrotoluene (T.N.T.), saccharine, and Congo red. By simply following the arrows backward we can trace the *ancestry* of each compound named. Thus the dyes at the bottom of the chart are all derived from aniline, but aniline is prepared from nitrobenzene and this from benzene, which is obtained directly from coal tar.

Properties and uses of important coal-tar compounds. It is possible to mention here only a few of the individual coal-tar compounds. We will simply note six compounds (Fig. 135) obtained directly from coal tar and a few typical compounds derived from each.

1. **Benzene** (C_6H_6). This is a colorless, highly inflammable liquid boiling at 80° . When treated with nitric acid *nitrobenzene* ($C_6H_5NO_2$) is formed, and this, on reduction, yields a nearly colorless liquid known as *aniline* ($C_6H_5NH_2$), from which hundreds of dyes of all colors are prepared.

2. **Toluene** (C_7H_8). This resembles benzene in appearance. When treated with nitric acid it forms the solid compound *trinitrotoluene* (T.N.T.), so largely used as an explosive in the World War. From toluene there are also prepared *saccharine*, a compound five hundred times as sweet as sugar, and *benzoic acid*, whose sodium salt, *sodium benzoate*, is our most common food preservative.

3. **Carbolic acid** (*phenol*) (C_6H_5OH). The pure acid is a white solid and is very poisonous. It serves for the preparation of *salicylic acid*, from which we prepare the well-known medicine *aspirin*. Carbolic acid is also used in the preparation of *picric acid* (a valuable explosive) and such substances as *bakelite* and *condensite*, used for making umbrella handles, pipestems, buttons, phonograph records, insulators in electrical devices, and many similar articles.

SOME COAL PRODUCTS

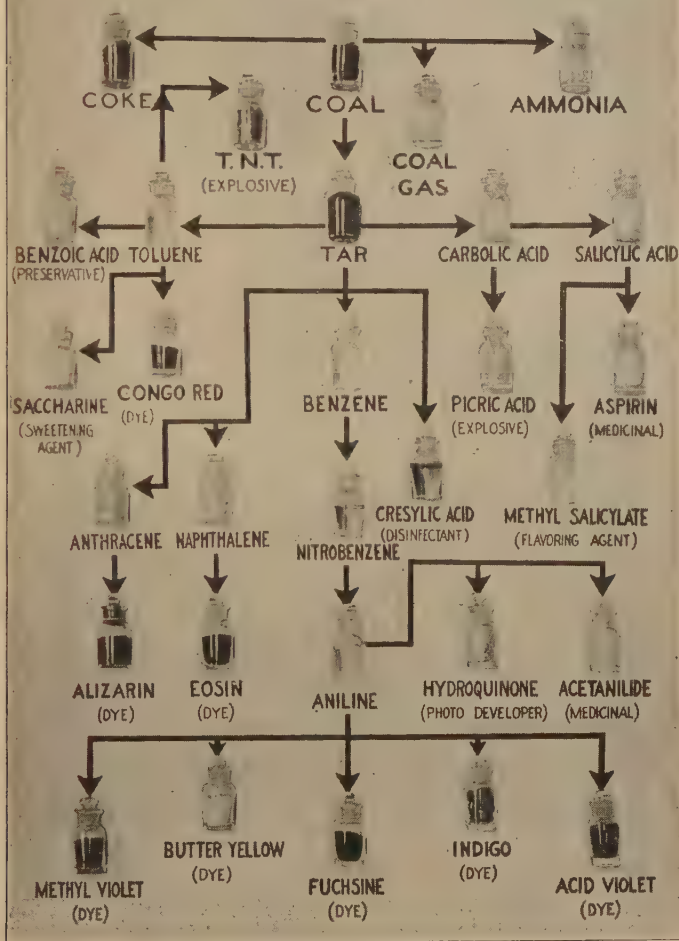


FIG. 136. Chart showing the derivation of some coal-tar compounds
(Suggested by Science Service)



FIG. 137. A case filled with American-made dyes
The picture above the case is that of William Henry Perkin, the discoverer of aniline dyes

4. *Cresylic acid* (C_7H_7OH). This substance is the basis of nearly all the common disinfectants used in our homes for such purposes as cleansing drainpipes and sinks.

5. *Naphthalene* ($C_{10}H_8$). This is a white crystalline compound, best known to us in the form of white balls commonly called *moth balls*.

6. *Anthracene* ($C_{14}H_{10}$). This is a nearly white solid and serves for the preparation of *alizarin*, one of our most valuable dyes.

Coal-tar dyes. All dyes derived from coal tar are known as *coal-tar* or *aniline dyes*. Many hundreds of these dyes have been prepared, of every imaginable color. It is interesting to note that two of the most common, namely, *indigo* and *alizarin*, were formerly obtained from vegetable sources. Chemists found out how to make them in the laboratory, and now they are made in this way at a much lower cost than formerly. The method of dyeing will be discussed in a later chapter.

Previous to the World War nearly all our dyes came from Germany. During the war this supply was cut off, and there was a temporary shortage of dyes. American chemists soon solved the problem connected with their production, and now the United States produces an adequate supply of dyes of the very highest grade (Fig. 137).

Historical. The first aniline dye was made in 1856 by an English boy seventeen years of age. His name was William Perkin. The boy was assisting in the laboratory of an English university, and during the holidays he spent his time trying to make *quinine*. In the course of some experiments with aniline he noticed that a colored substance of great beauty was produced. At this time all the dyes used were obtained from vegetable sources. Perkin got the idea that perhaps this new compound which he had prepared from aniline might be used as a dye. He finally succeeded in showing that it could be used and that it was superior to vegetable dyes in coloring power. This discovery led to others, and the investigation still continues, as shown by the fact that our dye

plants employ hundreds of chemists. It is interesting to note that in 1906, fifty years after Perkin's discovery, he came to the United States and attended a great meeting held in New York City in honor of the fiftieth anniversary of the discovery of the first aniline dye.

Coal-tar compounds in foods. Much discussion has arisen over the use of coal-tar compounds in foods. The Federal government has selected eight aniline dyes of different

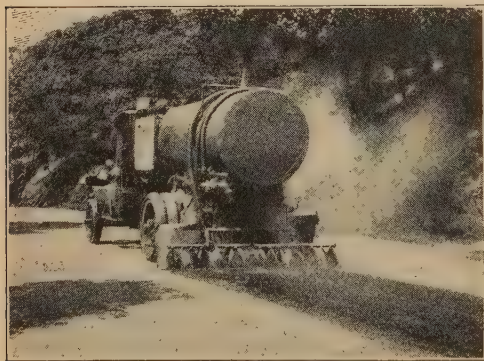


FIG. 138. Using pitch obtained from coal tar in road construction

colors the use of which is permitted in such foods as candies and butter. As already stated, the use of *sodium benzoate* as a preservative is allowed under certain restrictions. *Saccharine* was formerly permitted in foods, but in 1912 the government forbade the further use

of it. *Vanillin*, identical with the compound prepared from vanilla beans, and *coumarin*, which has an odor similar to vanillin, are both used in artificial vanilla extracts, but when they are so used the label on the container must state the fact. It is well to keep in mind that all such substances are not foods and are used for purposes other than nutrition.

Coal-tar compounds in medicines. Coal tar also furnishes us with many useful medicines. Among these are *acetanilide*, prepared by treating aniline with acetic acid and used in headache powders; *procaine*, a valuable local anæsthetic used in minor surgical operations and in extracting teeth; *stovaine*, also a local anæsthetic; *salicylic acid* and its derivative *aspirin*.

One of the most valuable of all these medicines is the compound known as *arsphenamine* (salvarsan). Many of our chemists are now working in the development of new compounds which promise to be of great service in the treatment of certain diseases that are now incurable.

Pitch and its uses. When coal tar is distilled there remains in the still a very thick, viscous, tarry mass known as *pitch*, which has extensive uses in road construction. Tar is frequently sprinkled on roadways to serve as a binder and thus prevent the wearing away of the road (Fig. 138).

EXERCISES

1. Are all the so-called coal-tar compounds present in coal tar?
2. (a) What is the difference in composition between benzene and benzine? (b) Have the two substances any properties in common?
3. Do you see any reason why benzene could not be used in place of gasoline in a gasoline engine?
4. Trace the steps in obtaining aspirin from coal tar (Fig. 136).
5. Mention four important compounds prepared from toluene and the uses of each.
6. Trace the steps in obtaining indigo from coal tar.
7. Mention five different compounds obtained from coal tar, each used for a different purpose, and state the use of each (Fig. 136).
8. Mention a dye and an explosive, both of which are prepared from the same compound. Does this suggest a reason why the Germans used their dye factories for making explosives during the World War?
9. What do you think of the propriety of allowing foods to be colored artificially?
10. Calculate what weight of benzene will be required to make 100 kg. of aniline, assuming that 1 gram-molecule of benzene will give 1 gram-molecule of aniline, thus:



CHAPTER XXVI

CARBOHYDRATES AND TEXTILES

Carbohydrates. The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, the last two elements usually being present in the proportion in which they combine to form water. The most important carbohydrates are the following:

TABLE OF CARBOHYDRATES

Sucrose (ordinary sugar)	$C_{12}H_{22}O_{11}$
Lactose (milk sugar)	$C_{12}H_{22}O_{11}$
Maltose	$C_{12}H_{22}O_{11}$
Dextrose (grape sugar)	$C_6H_{12}O_6$
Levulose	$C_6H_{12}O_6$
Dextrin	$(C_6H_{10}O_5)_x$
Cellulose	$(C_6H_{10}O_5)_x$
Starch	$(C_6H_{10}O_5)_x$

The molecular formulas of dextrin, cellulose, and starch are unknown, but are multiples of the simple formula $C_6H_{10}O_5$; hence they are often written $(C_6H_{10}O_5)_x$. In the discussion of the compounds they will be represented by the formula $C_6H_{10}O_5$.

It will be noted that some of the compounds named in the above table have the same formula. *Compounds having the same formula are said to be isomeric. The difference in the properties of such compounds is due to the fact that the atoms are arranged differently in the molecule.* Just as two houses may be entirely different and yet each be built from the

same kind and the same number of brick, so two compounds may be different, and yet the molecule of each contain the same elements and the same number of atoms of each.

Sucrose (sugar) ($C_{12}H_{22}O_{11}$). This substance, commonly called *sugar*, occurs in many plants. The world's supply comes entirely from the sugar cane and the sugar beet, the sugar cane



FIG. 139. Source of the world's output of sucrose, — the sugar cane and the sugar beet

furnishing about 70 per cent of the total output. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers); the sugar beet thrives in cooler climates (Fig. 139), such as prevail in Germany or in Ohio and Michigan in the United States. The beets contain as high as 16 per cent of sucrose.

The separation and refining of sugar. To obtain the sugar from the sugar beet, the beets are sliced and then placed in large cylindrical containers. Water is run through these containers and dissolves the sugar in the beets. Unfortunately it also dissolves

many other substances present, so that the chemist must find ways for removing these impurities. This is done partly by precipitation and partly by filtering through some porous material such as bone-black. The resulting solution is then evaporated in closed vessels (vacuum pans *A*, Fig. 140) from which the air is partially exhausted. In this way the boiling point of the solution is lowered and the charring of the sugar prevented. After the sugar crystallizes out it is separated from the remaining sirup by transferring it to perforated vessels which are whirled at a high rate of speed (centrifugals) (Fig. 141). The sugar is separated from the juice of the sugar cane by making use of the same general principles.

The impurities in the beet juice are more distasteful than those in the cane juice, hence all beet sugar must be highly refined. Ordinary brown sugar is cane sugar only partially refined. It is not practicable to separate all the sugar from its solution. The sirup that remains when sugar is prepared from sugar cane constitutes ordinary *molasses*. The sweetness of maple sugar and maple sirup is due to sucrose, other products present in the maple sap imparting the distinctive flavor. Cane sugar and beet sugar, *when pure*, are identical, and even the chemist cannot distinguish between them. The annual consumption of sugar in the United States amounts to nearly 100 lb. for each person.

Chemical conduct of sucrose. When a solution of sucrose is heated to about 70° with water and hydrochloric acid, the sugar and water react to form two isomeric sugars, *dextrose* and *levulose*, as shown in the equation



In this process the sugar is said to be *inverted*, and the mixture of dextrose and levulose is called *invert sugar*. These two sugars are white solids. They are not so sweet as sucrose, neither do they crystallize so easily; hence in making candy from sucrose it is customary to add a small amount of acid (vinegar) or acid salt (such as cream of tartar), which produces some invert sugar, whose presence prevents the remaining sucrose from crystallizing.

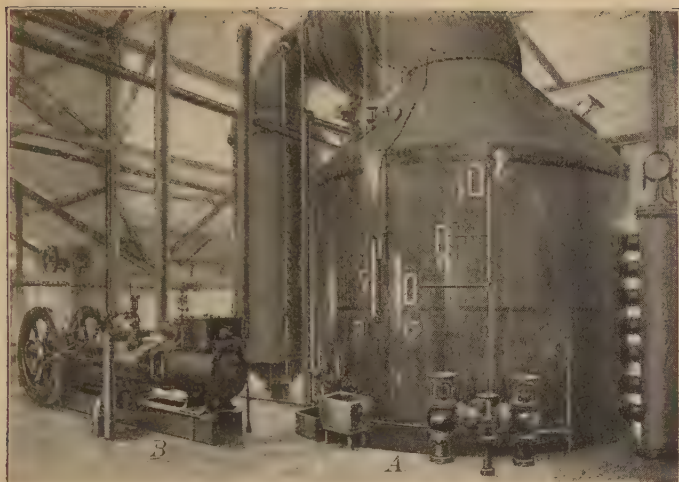


FIG. 140. Vacuum pans in a sugar factory
The air is pumped from the pans *A* by the engine *B*

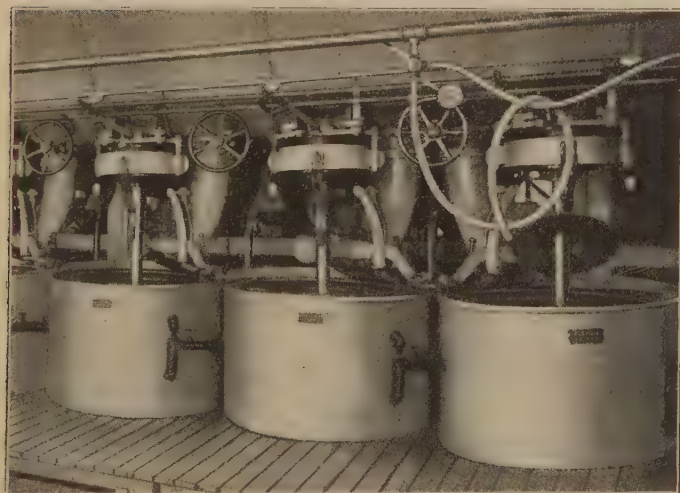


FIG. 141. Centrifugals for removing the sugar from sirup

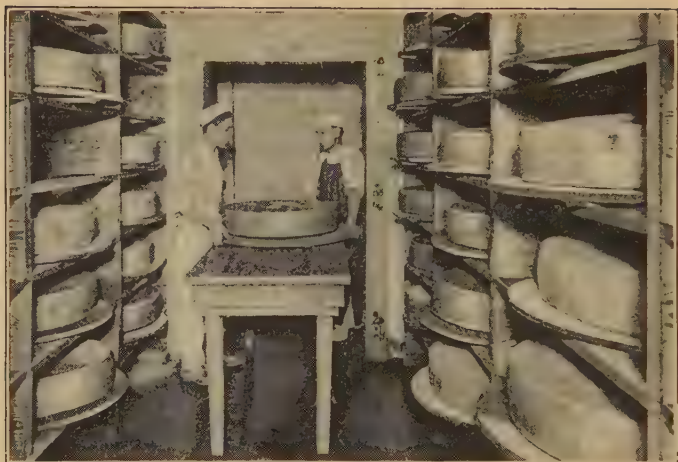


FIG. 142. Cheese stored for "ripening"



FIG. 143. Making glucose (corn sirup)

Starch and a little hydrochloric acid are heated with steam in a large copper vessel *A*, which is known as a "converter"

When heated to 160° sucrose melts; if the temperature is increased to about 215° a partial decomposition takes place and a brown substance known as *caramel* is formed. This is used extensively as a coloring matter and in making confectionery.

Lactose (milk sugar) ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). This compound is a white solid, but is not so sweet or so soluble as sucrose. It is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water	87.17%
Casein (nitrogenous matter)	3.56%
Butter fat	3.64%
Lactose	4.88%
Mineral matter	0.75%

The casein is a solid and is present in sweet milk in a finely divided state. When the milk sours, the casein separates. The remaining liquid, known as *whey*, contains the lactose, which can be obtained by evaporation. The souring of milk is due to the fact that the lactose present changes into *lactic acid*, a liquid having the formula $\text{C}_3\text{H}_6\text{O}_3$.



This change is brought about through the agency of a certain microörganism which enters from the air, and the process is known as *lactic fermentation*. The body of the ordinary medicine tablet consists of lactose because this substance readily absorbs medicinal solutions.

The souring of milk. It has been stated that the souring of milk is caused by a certain microörganism. This organism is really a microscopic plant which grows in the milk, and in so doing changes the lactose into lactic acid. The plant does not grow at low temperatures; hence the souring of milk is prevented (or delayed) by keeping it cold. Extreme cleanliness also tends to retard souring by preventing the introduction of the plant, the spores of which are present in filthy matter.

The pasteurization of milk. Certain diseases may be spread by impure milk just as by impure water (p. 66). The microorganisms which cause these diseases may be killed by boiling the milk as in the case of water. This process, however, causes changes in the milk which impair its food value. The same results can be accomplished, without impairing the food value of the milk, by heating it to about 65° for forty minutes. Such milk is said to be *pasteurized*,



FIG. 144. When rennet is added to milk the casein separates (or sets) in the form of a porous solid

the term being derived from the name of the great French chemist Pasteur, who first showed that many changes and diseases are due to microorganisms.

The making of cheese. Cheese is made from the casein of milk. Ordinarily

the fat of the milk is left in with the casein (cream cheese). To separate the casein there is added to the milk a substance known as *rennet*, which is extracted from calves' stomachs. When the rennet is added to the milk it causes the casein to separate (or set) in the form of a porous solid, which contains the other ingredients of the milk in its pores. After the casein sets (Fig. 144) it is cut by knives and separated from the whey. The resulting casein is then salted, compressed in molds, and set away in a cool place for several weeks to ripen (Fig. 142). In this process certain changes take place which produce small percentages of compounds which impart to the cheese its characteristic taste. These changes are brought about by microorganisms, and each kind of organism produces definite changes. By inoculating the newly made cheese with

the proper microörganism it is possible to secure the desired flavor, or, in other words, to prepare the kind of cheese desired.

Maltose. When certain grains, like barley, start to grow, the sprouting grains develop a substance known as *diastase*, which has the power of changing starch into a sugar known as *maltose*. *Malt* (Fig. 145) consists of barley grains which have been kept in a moist, warm place until the grains germinate and have then been heated to destroy the vitality of the germ. The malt contains diastase and is used for converting starch into maltose in the preparation of alcohol. The diastase acts as a catalytic agent.

Dextrin. This is a sweetish solid obtained by roasting starch under proper conditions; hence it is present in toast and bread crust. It is soluble in water and has many uses, such as making gum, mucilage, and paste. It is used on the back of postage stamps and stickers of all kinds.



FIG. 145. Malt used in preparing maltose

Dextrose (grape sugar) ($C_6H_{12}O_6$). This sugar is present in honey and in many fruits, usually associated with levulose, and is often called *grape sugar*, because of its presence in grape juice. It can be obtained, along with levulose, by heating sucrose with hydrochloric acid, as explained on page 240. Commercially it is prepared by heating starch and water with a small percentage of hydrochloric acid.



When the change is complete the hydrochloric acid is neutralized by sodium carbonate and the solution is evaporated.

Glucose (corn sirup). When starch and water are heated with hydrochloric acid (catalytic agent) pure dextrose is obtained, as stated above. If the process is stopped short of completion the product consists of dextrose, maltose, and dextrin, sufficient water

being present to form a thick, colorless sirup. This product is known as *glucose*. Enormous quantities of it are prepared. The starch used in its preparation is obtained from corn, about 65,000,000

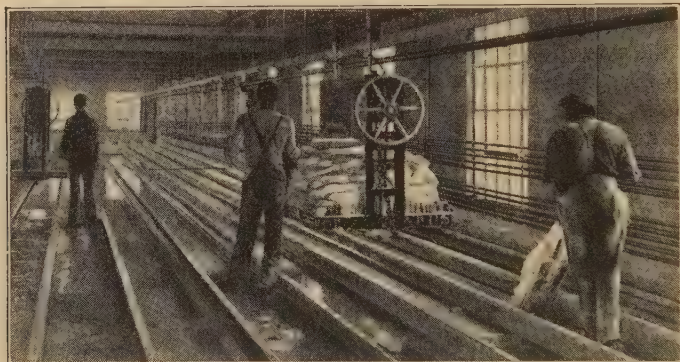


FIG. 146. Removing the starch from the settling troughs in a starch factory

bushels of corn being used yearly for this purpose. The starch, water, and acid are introduced into large copper retorts (*A*, Fig. 143) fitted with steam pipes and heated under pressure with live steam.

Glucose is much cheaper than sugar and is used chiefly in making candy, jellies, jams, and table sirups. One brand of *corn sirup*, largely used, consists of 85 per cent of glucose and 15 per cent of molasses, the latter being added to impart the flavor.

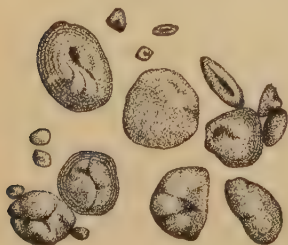


FIG. 147. Wheat-starch granules magnified 200 diameters

Starch ($C_6H_{10}O_5$). This substance is always present in seeds and tubers and is one of the abundant carbohydrates found in nature. In

the United States it is obtained chiefly from corn, about 60 per cent of which is starch; a limited supply is obtained from potatoes. In Europe, on the other hand, the potato serves as the principal source.

Manufacture of starch. In manufacturing starch from corn, the corn is first soaked in water containing a little sulfurous acid to soften the grain. It is then ground coarsely so as not to crush the germ. When the resulting mass is mixed with water the germ floats, being very light because of the oil which it contains. In this way the germ is separated from the rest of the seed, and from it *corn oil* is prepared. The remaining material, consisting of the starch, the nitrogenous constituent (gluten), and the bran, or outside coating of the grain, is then ground fine, mixed with water, and passed through cloth sieves, which remove the bran. The water containing the starch and gluten in

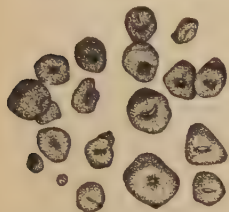


FIG. 148. Granules of cornstarch magnified 200 diameters

suspension is then allowed to run slowly down long, shallow troughs, the rate of flow being regulated so that the heavier starch sinks to the bottom of the trough while the lighter gluten is washed away. The starch is then removed from the troughs (Fig. 146) and dried. Large quantities of starch are used in making glucose and other foods, for finishing cloth, and for laundry purposes.

Characteristics of starch. Starch consists of minute granules which differ somewhat in appearance, according to the source of the starch, so that it is often possible from a microscopic examination to determine from what plant any given sample of starch was obtained (Figs. 147 and 148). When heated with water the granules burst and the starch partially dissolves. This is the reason why starchy foods are made more digestible by cooking.



FIG. 149. Two very important derivatives of cellulose

Cellulose ($C_6H_{10}O_5$). Cellulose is the basis of all wood fibers. Cotton and linen are nearly pure cellulose. Cellulose is insoluble in water and dilute acids, but dissolves in a solution



FIG. 150. Section of movie film made of nitrocellulose

prepared by dissolving copper oxide in ammonium hydroxide. Concentrated hydrochloric acid changes it into dextrose. A mixture of sulfuric and nitric acids acting upon it forms a number of compounds collectively known as *nitrocellulose* or *guncotton* (Fig. 149). These are white solids, but they can also be obtained in a transparent form (Fig. 150). They are inflammable and, under certain conditions, highly explosive. They are the chief constituents of most *smokeless powders*. Photographic films (Fig. 150) are made from them, as well as from a derivative of cellulose known as *cellulose acetate*, which is not so inflammable as nitrocellulose. *Collodion* is a solution of nitrocellulose in a mixture of alcohol and ether. *Celluloid* is a mixture of nitrocellulose and camphor (a white solid obtained from the camphor tree, which grows in Japan). These two, when mixed together, form a plastic mass which can be molded into any desired shape and which is used for making such objects as combs and brush handles. When such articles are warmed by holding them between the hands, the odor of camphor is easily detected. Nitrocellulose is also used in making a sort of artificial leather (*fabrikoid*), from which handbags and trunks are made.

Natural silk. Silk has long been known and highly prized, as is shown by the references to it in the Bible. The silk fiber is spun by

the silkworm. These are grown in large numbers (Fig. 151), especially in Japan and China, and utilized in the production of silk.

Mercerized cotton and artificial silk. When cotton cloth is treated with a concentrated solution of sodium hydroxide, the cellulose shrinks and becomes tougher in character. If the cloth is placed



FIG. 151. The production of natural silk

The silk is spun by the silkworm. The worm (*B, B, B*) feeds best on mulberry leaves. When ready to spin it fastens itself by threads to the branches of the tree (*C*) and spins silk fibers (often 1000 yards in length) about its body, forming the cocoon (*D, E*). In this process the worm is gradually transformed into the *chrysalis* (*F*), then into the *insect*, which breaks through the cocoon (*G*) and becomes free. The insect (*A*) lays the eggs from which the worm is hatched, and the cycle repeats itself. The threads forming the cocoons are wound onto reels and are used for weaving silk fabrics

in stretchers to prevent the shrinkage, it assumes an appearance somewhat resembling silk and is known as *mercerized cotton*. Another fabric prepared in large quantities from cellulose resembles silk very closely and is known as *artificial silk* (Fig. 152).

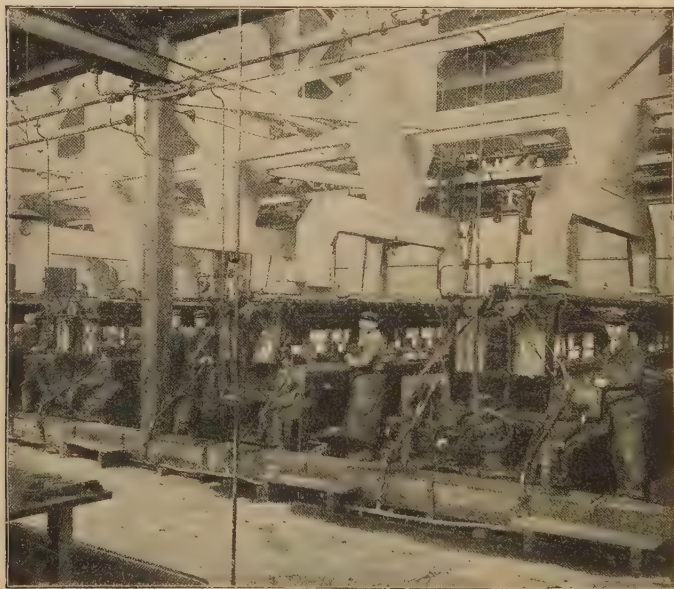


FIG. 152. The production of artificial silk (viscose) in a French factory

Cellulose or one of its derivatives is dissolved, and the concentrated solution is forced through minute tubes and received into appropriate liquids which cause the cellulose to coagulate in the form of fine threads. France is a leader in the production of artificial silk, but the United States also produces a large amount. Artificial silk resembles natural silk in appearance, but is not so strong. (From Duncan's "Chemistry of Commerce")

Characteristics of various textile fibers. Of the different fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are composed of nitrogenous substances. Although these fibers resemble each other when viewed with the naked eye, their

appearance varies widely when examined with the microscope (Fig. 153). It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide (5 per cent to 10 per cent) has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk. The nitrogenous fibers burn with a foul odor like that of burning hair, and this property is sometimes useful in determining the source of a fiber.



FIG. 153. Textile fibers (highly magnified)

Paper. Paper consists mainly of cellulose, the finer grades being made from linen and cotton rags and the cheaper grades from wood.

Manufacture of paper. Most of our paper is made from wood. The trees, such as spruce and hemlock, are cut down, floated down to the mills, and there sawed into short lengths. The bark is then removed and the wood cut into small chips by allowing the short lengths to slide down a trough against a rapidly revolving wheel fitted with sharp blades. The resulting chips are then placed in large retorts and heated either with a solution of sodium hydroxide or with calcium acid sulfite (a compound prepared by passing sulfur dioxide upwards through large towers filled with limestone, over which water trickles); these dissolve the objectionable matter from the wood, leaving the cellulose, which is then bleached with chlorine and washed with water. The cellulose is thus obtained in the form of thin shreds suspended in water, and this is known as *paper pulp*. This pulp (A, Fig. 154) is run onto wire screens, and most of the water present runs through the screen. It then passes between large iron cylinders, some of

which are heated with steam. In this way the pulp is pressed and dried and delivered in the form of paper (*B*, Fig. 154). In the process different materials are often added to the pulp. These vary with the nature of the paper desired; thus finely ground clay or calcium sulfate is added to give body to the paper. In making paper intended for writing or printing, a compound prepared by heating resin and sodium hydroxide is added, together with aluminium sulfate. This prevents the ink from spreading.

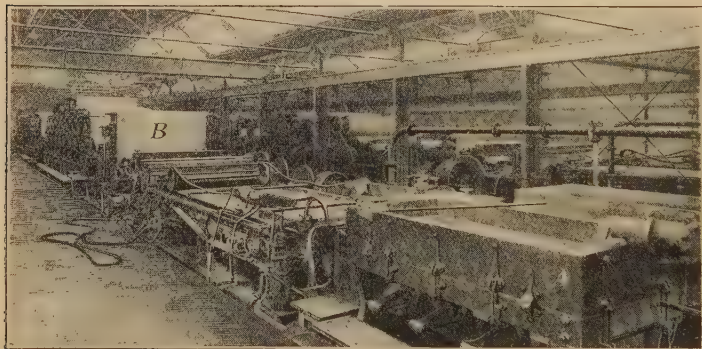


FIG. 154. View of the interior of a paper mill

The alkaloids. We have seen in this chapter that plants furnish us with food and clothing. They also furnish us with many useful medicines. Prominent among these is the class of substances known as *alkaloids* because of their basic properties. Each of these is found in some part of a certain plant. Thus *caffeine* is always present in the coffee berry and tea leaves and is their active constituent. Some of the most important alkaloids are *quinine*, *morphine*, *strychnine*, and *cocaine*. All the above are white, solid compounds containing carbon, hydrogen, oxygen, and nitrogen. *Nicotine*, the active constituent of tobacco, is one of the few liquid alkaloids.

The alkaloids, as a rule, are very active, and most of them are intensely poisonous. Some of them, especially cocaine and morphine, are very dangerous habit-forming drugs.

EXERCISES

1. What is the relation between the number of atoms of hydrogen and oxygen in each of the carbohydrates given in the table on page 238.
2. Distinguish between the two terms *allotropic* and *isomeric*.
3. (a) Is there any difference between unrefined cane sugar and unrefined beet sugar? (b) between refined cane sugar and refined beet sugar?
4. It is sometimes stated that milk sours more readily during thunderstorms. Do you think there is any evidence for the truth of this statement?
5. What constituents of milk are used in the making of cheese?
6. To what is (a) the sweet taste of milk due? (b) the sour taste?
7. Why do different kinds of cheese have different flavors?
8. What is the function of the hydrochloric acid used in making glucose?
9. Is any constituent of toasted bread soluble in water?
10. Enumerate the uses of cellulose.
11. How could you distinguish (a) between artificial and natural silk? (b) between mercerized cotton and silk?
12. Celluloid is readily inflammable. What is the combustible constituent present in it?
13. Can you suggest any chemical change that may take place when starched clothes are ironed?
14. What weight of starch is necessary for the preparation of 100 kg. of dextrose?
15. What weight of invert sugar can be prepared from 100 g. of sucrose?

CHAPTER XXVII

ALCOHOLS; PRESERVATIVES

The alcohols. Just as there are a great many sugars, so there are a great many alcohols. The two most important ones are *methyl alcohol* (CH_3OH) and *ethyl alcohol* ($\text{C}_2\text{H}_5\text{OH}$). The latter compound is the common alcohol. Both of these alcohols are colorless, inflammable liquids.

Methyl alcohol and ethyl alcohol may be regarded as derived from methane (CH_4) and ethane (C_2H_6) by substituting an OH group for an atom of hydrogen; hence the terms *methyl* and *ethyl*.

Methyl alcohol (wood alcohol) (CH_3OH). This compound is formed when wood is heated in the absence of air (p. 106), and on this account it is called *wood alcohol*. It is a colorless liquid which boils at about 66° and burns with an almost colorless flame. It is a good solvent for organic substances and is used extensively in the manufacture of varnishes. It is quite poisonous, and many deaths occur from its use as a substitute for ethyl alcohol. It acts upon the optic nerve, and many persons have become blind from drinking the liquid or from repeatedly inhaling its vapor.

Duncan states that "out of 10 men who drink 4 oz. of pure methyl alcohol in any form whatever, 4 will probably die, 2 of them becoming blind before death. The remaining 6 may recover, but of these, 2 will probably be permanently blind."

When a mixture of the vapor of methyl alcohol and air is passed over hot copper, the alcohol is partially oxidized, forming a gaseous compound known as *formaldehyde*:



This gas is now prepared in large quantities and used as a disinfectant and also to prevent decay. A 40 per cent aqueous solution of it is sold under the name *formalin*.

Ethyl alcohol (grain alcohol, alcohol) (C_2H_5OH). This compound is the one commonly known as alcohol. It is a colorless liquid with a pleasant odor and is an excellent solvent for many organic substances. It boils at 78.3° . It is sometimes used as a fuel, since its flame is very hot and does not deposit carbon, as the flame from oil does. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The intoxicating properties of such liquors as wine and whisky are due to the alcohol present. The ordinary alcohol of the druggist contains about 95 per cent of alcohol and 5 per cent of water. A solution containing 99 per cent or more of alcohol is called *absolute alcohol*. When alcohol is heated with sulfuric acid a low-boiling inflammable liquid known as *ether* is formed:



This is largely used as an anæsthetic in surgical operations.

Preparation of ethyl alcohol. Alcohol is prepared by the action of ordinary baker's yeast upon different sugars such as dextröse:

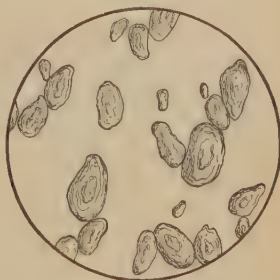


FIG. 155. Some cells of the yeast plant (magnified)

This process in which a sugar is changed into alcohol and carbon dioxide by the action of yeast is known as *alcoholic fermentation*. The yeast is a low form of plant life (Fig. 155) and thrives in appropriate sugar solutions. During its growth a number of changes take place which result in converting the sugar into alcohol and carbon dioxide, as is shown in the above equation.

Alcohol can also be prepared by adding yeast to a solution of sucrose. The sucrose is first changed into dextrose and levulose (invert sugar, p. 240) by the yeast. The dextrose and levulose then ferment.

Commercial preparation of alcohol. Most of the alcohol made in the United States for commercial purposes is prepared from crude molasses, which is brought from Cuba in large quantities for this purpose and directly fermented. A limited amount is made from starch obtained from corn. When starch is used it is first mixed with *malt* (p. 243), which changes the starch into maltose. Yeast is then added, and the maltose ferments. The alcohol is separated by fractional distillation.

The alcohol problem. From very ancient times men of all nations have prepared alcoholic liquors of various kinds as beverages. In alcoholic content these range from 3 to 5 per cent in beers and light wines to 50 per cent and higher in whisky and brandy. Governments have found these beverages to be a fruitful source of revenue and have imposed heavy taxes on all kinds of fermented and distilled liquors, carefully supervising their manufacture. They have also taxed pure alcohol heavily because imitation beverages can be made very easily from pure alcohol. In this country the Federal government imposed a tax on 95 per cent alcohol, which before the war was \$2.10 per gallon and since the war \$4.20 per gallon.

On the other hand, alcohol has important scientific and industrial uses for which no good substitute can be found, and the government has no desire to interfere with these uses, which the Federal prohibition act defines very carefully. Accordingly, educational and scientific institutions can obtain alcohol tax free for scientific uses, and for industrial purposes the government allows the use of *denatured* alcohol free of tax. Denatured alcohol is alcohol to which has been added a definite amount of some substance which renders it unfit for use as a beverage

but which does not impair its use for manufacturing purposes. The substances which may be added for this purpose are prescribed by law and are known as *denaturants*. The most common denaturant is *pyridine*, a vile-smelling substance obtained by heating bones in the absence of air.

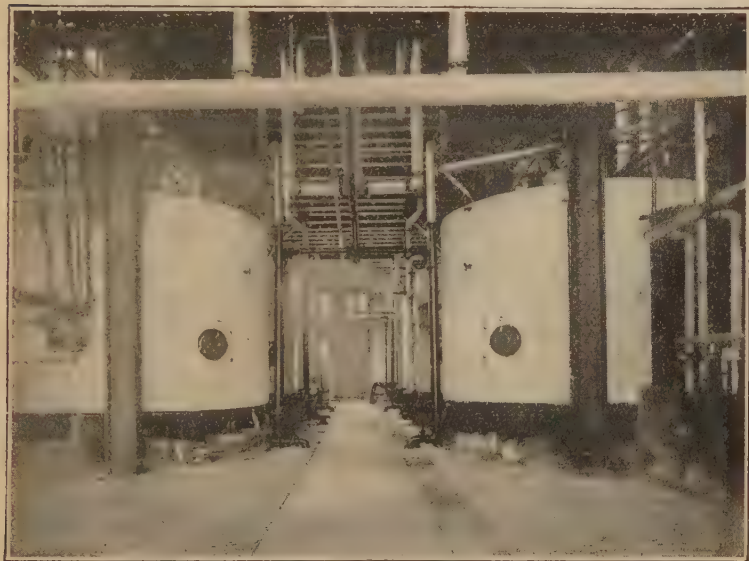


FIG. 156. Interior view of an industrial alcohol plant
Distilling off the alcohol

Soft drinks (pop). The soft drinks on the market consist of water charged with carbon dioxide, sweetened with sugar or glucose, and flavored with various substances such as vanillin and the oils obtained from lemon and orange peeling. Oftentimes they contain a small amount of citric or tartaric acid (pp. 261, 262). A few of them contain *caffeine* (p. 250), which is the active constituent of tea and coffee. The colored ones contain aniline dyes, as can easily be proved by heating a highly colored pop for five or ten minutes with a strip of white woolen fabric. The dye leaves the liquid and dyes the wool a brilliant color.

Enzymes. We will recall that malt (p. 243) contains a substance known as *diastase*, which has the property of changing starch into a sugar. This diastase belongs to a class of substances known as *enzymes*. There are many enzymes, and they often are of great importance. Thus yeast produces the enzyme known as *zymase*, and it is the zymase which really changes the sugar into alcohol and carbon dioxide. Yeast, therefore, is a sort of manufacturing plant for the production of zymase. It also produces an enzyme known as *invertin*, which changes sucrose into invert sugar. Enzymes play an important part in the process of digestion. For example, the active principle of the gastric juice is the enzyme *pepsin*. We know little about the chemical nature of enzymes. They are produced by growing organisms and seem to act as catalytic agents.

Chemical changes in bread-making. The average composition of wheat flour is as follows:

Water	11.9%
Gluten (nitrogenous matter)	13.3%
Fats	1.5%
Starch	72.7%
Mineral matter	0.6%

In making bread, flour is mixed with water, yeast, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. In baking bread the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become porous and making the bread light.

Preservatives. We have observed that the changes taking place in the souring of milk and the changing of sugar into alcohol are caused by microorganisms, the cells of which are

present in the air. Many other similar changes, such as putrefaction (decay), are due to the same causes. All these changes may be prevented in one of the following ways:

1. By keeping the substance at such a low temperature that the organism causing the change cannot thrive (cold storage).

2. The substance may be heated so as to destroy all organisms present and then sealed air-tight in a suitable container. This is the method used in canning vegetables. Foods treated in this way are said to be *sterilized*.

3. Some substance may be added which in small amounts will destroy the organisms causing the change or will prevent their growth. Such a substance is known as a *preservative*.

Whether or not preservatives should be permitted in foods is a much debated question. Some people maintain that any substance which is powerful enough to prevent the growth of the organisms must have an injurious action upon digestion. The Federal government at present allows the use of *sodium benzoate* (p. 234) in such foods as jellies, jams, and catchup, which are not consumed immediately upon the opening of the container. If this preservative is used, however, the labels on the containers must state the amount present.



FIG. 157. Sterilizing canned corn

Fig. 157 shows the method used in sterilizing canned corn in a large factory. The cans are filled with corn and are then placed in a large wire basket A, of such a size as to fit into the retorts (1, 2), a number of which are shown in the figure. When the

retort is filled the lid is clamped on and the corn heated by leading live steam into the retort. A small opening is left in the cans during the heating so as to allow for the escape of air. When the corn has been heated long enough to destroy all microorganisms, the cans are removed and the opening sealed under conditions that prevent the admission of any air.

EXERCISES

1. How could you distinguish between methyl alcohol and ethyl alcohol?

2. What is the name of the process used in separating alcohol from water?

3. Give the changes involved in making alcohol from corn.

4. Why is a little sugar or molasses added in making bread?

5. For what purpose is yeast always used?

6. Distinguish between lactic fermentation and alcoholic fermentation.

7. Why does the government permit the use of a preservative (sodium benzoate) in tomato catchup but not in milk?

8. Suggest a method for making alcohol from sawdust.

9. What compounds have we studied that are used as anæsthetics?

10. It has been proved that automobiles may be run by alcohol in place of gasoline. What is the objection to its use for this purpose?

11. (a) What are the products of combustion of alcohol? (b) Write the equation for the reaction that takes place when it burns.

12. (a) Is alcohol formed in making bread? (b) Does the finished product contain any alcohol?

13. How could you prevent (a) sweet cider from becoming hard? (b) grape juice from becoming wine?

14. What weight of dextrose is necessary for the preparation of 100 kg. of the alcohol of the druggist, assuming that 95 per cent of the dextrose ferments?

15. What weight of pure methyl alcohol is necessary for the preparation of 1 kg. of formalin? (Formalin contains 40 per cent by weight of formaldehyde.)

CHAPTER XXVIII

ORGANIC ACIDS AND THEIR DERIVATIVES; PROTEINS

Organic acids. A great number of acids are known which are composed of carbon, oxygen, and hydrogen, and as a group these are called *organic acids*. Like the hydrocarbons, they can be arranged in series, one of the most important of which is known as the *fatty-acid series*. A few of the most important acids of this series are given in the following table. They are all monobasic — a fact indicated in the formula by separating the replaceable hydrogen atom from the rest of the molecule.

SOME FATTY ACIDS

$\text{H} \cdot \text{CHO}_2$		formic acid, a liquid boiling at 100°
$\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$		acetic acid, a liquid boiling at 118°
$\text{H} \cdot \text{C}_4\text{H}_7\text{O}_2$		butyric acid, a liquid boiling at 163°
$\text{H} \cdot \text{C}_{16}\text{H}_{31}\text{O}_2$		palmitic acid, a solid melting at 62°
$\text{H} \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$		stearic acid, a solid melting at 69°
$\text{H} \cdot \text{C}_n\text{H}_{2n-1}\text{O}_2$		general formula

Of these acetic acid deserves special mention.

Acetic acid ($\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$). This is the acid which imparts the sour taste to vinegar. It is prepared commercially by the destructive distillation of wood (p. 106). It is a colorless liquid and has a strong, pungent odor. When anhydrous it crystallizes as a white solid which melts at 18° and closely resembles ice in appearance; hence the name *glacial acetic acid*. Many of the salts of acetic acid (*acetates*) are well-known compounds. Thus lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$) is the white solid known as *sugar of lead*.

Vinegar. As is well known, when cider is exposed to the air it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider first undergoes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic acid, the necessary oxygen coming from the air. This oxidation is brought about through the action of a microörganism present in the so-called *mother of vinegar*. The oxidation of alcohol into acetic acid through the agency of the organism is known as *acetic fermentation* and may be represented as follows:

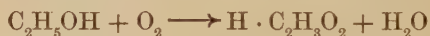


FIG. 158. A generator for the manufacture of vinegar

Manufacture of vinegar. The old method of making vinegar consisted simply in storing cider in barrels until the fermentation was complete—a process requiring several weeks. In the modern method the change is brought about in a few hours, a large cask known as a *generator* being used (Fig. 158). This is filled loosely with beech shavings. Vinegar is first sprayed into the top of the cask in order to introduce the *mother of vinegar*. The organism present attaches itself to the shavings, which are used because they present a large surface. Next a dilute solution of alcohol (*hard cider*, in the case of cider vinegar) is sprayed into the top of the cask while air is admitted at the bottom *A, A*. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom *B* of the cask. Instead of starting with cider, one may use almost any substance which contains starch or sugar, these compounds first being changed into alcohol, as explained in the manufacture of alcohol. In this way are prepared *malt vinegar* from starch and *sugar*

vinegar from sugar residues. The cheapest vinegar is made from pure dilute alcohol and is known as *distilled vinegar*. It is colorless and leaves no residue upon evaporation.

The Federal law requires that all vinegar shall contain not less than 4 per cent of acetic acid. In addition to the acid, vinegar prepared from fruits and grains contains certain solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

The question might arise as to why it is not possible to make vinegar by simply adding to water the necessary percentage of acetic acid obtained from the distillation of wood. Such a product could be made at low cost and would be just as sour as vinegar; however, it would not have the odor or flavor of vinegar. This is due to the fact that when acetic fermentation takes place, there are formed, in addition to acetic acid, small percentages of other compounds, and it is these which impart to vinegar its characteristic flavor and odor.

Acids belonging to other series. In addition to the fatty acids, the following deserve special mention:

Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). This is a white solid and is found in a number of plants.

Malic acid ($\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_5 \cdot \text{H}_2\text{O}$). This acid occurs in apples, pears, and some other fruits.

Tartaric acid ($\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$). This is a white solid and occurs in many fruits either in the free state or in the form of its salts. The acid potassium salt ($\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$) occurs in the juice of grapes. When the juice ferments in the manufacture of wine, this salt, being insoluble in alcohol, separates on the sides of the cask, and in this form is known as *argol* (Fig. 159). When purified it forms a white solid, which is sold under the name of *cream of tartar* and is used in baking-powders. The acid itself is often used in soft drinks.



FIG. 159. Argols, the source material of cream of tartar

Citric acid ($\text{H}_3 \cdot \text{C}_6\text{H}_5\text{O}_7$). This acid occurs in the so-called citrous fruits, such as the lemon and grapefruit. It is a white solid, soluble in water, and is often used as a substitute for lemons in making lemonade.

Oleic acid ($\text{H} \cdot \text{C}_{18}\text{H}_{33}\text{O}_2$). The derivatives of this acid constitute the principal part of many oils and liquid fats. The acid itself is an oily liquid.

Fats and oils. The hydrogen of acids can be replaced not only by metals but by *hydrocarbon radicals* (such as CH_3 and C_2H_5) as well. The resulting compounds are termed *esters*. Some of



FIG. 160. The three chief constituents of oils and fats

these esters have a pleasant fruity odor and are used as flavoring agents. The main constituents of the common fats and oils, such as butter, lard, and olive oil, are esters of *oleic*, *palmitic*, and *stearic acids* and are known respectively as *olein*, *palmitin*, and *stearin* (Fig. 160). The radical present in these esters is C_3H_5 . It is

tervalent and is known as the *glyceryl* radical, since it is present in *glycerin* ($\text{C}_3\text{H}_5(\text{OH})_3$). Since the glyceryl radical is trivalent, and since oleic, palmitic, and stearic acids are all monobasic, it is evident that three molecules of each acid must enter into the formation of each molecule of the ester derived from it. The relation in composition between these acids and the corresponding esters is shown in the following formulas:



Olein is a liquid and is the main constituent of oils such as olive oil. Palmitin and stearin are white solids and are the chief constituents of the solid fats. Beef suet is principally stearin.

The oils and fats are widely distributed in the animal and vegetable kingdoms. Almost every seed and fruit as well as the tissues of animals contain oil which can be removed by pressure. Thus we have olive oil, corn oil, cottonseed oil, coconut oil, palm oil, lard oil, fish oil, and a host of others. In separating these from the source material we are sure to obtain along with the oil some other substances dissolved in the oil. Sometimes these substances add to the flavor, as is the case with olive oil. More often they impair its looks and taste. Chemists have succeeded in finding ways for removing these impurities, and the oils when so refined are very much alike in composition. Thus the refined cottonseed oil is now largely used for the table in place of the more expensive olive oil.

Changing oils into solid fats: the hydrogenation of oils. It will be noted that stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule. Now if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalytic agent (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. It is possible in this way to change the oils into solid fats. Certain commercial fats used in cooking, mostly sold under trade names, are made by this process from the comparatively inexpensive cottonseed oil.

The cottonseed-oil industry. Cotton seeds are bulky, and formerly it was a source of expense to dispose of them. One of the functions of chemists is to find uses for apparently useless substances, and they soon discovered that cotton seeds contain a valuable oil. In place of being a source of expense, cotton seeds are now the source of over one billion pounds of oil annually, worth many millions of dollars.



A cotton plantation in the South, as shown in A. The cotton is picked by hand and placed in large baskets



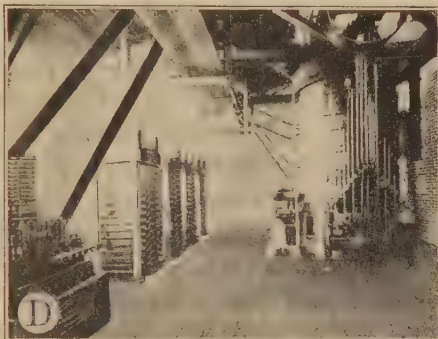
After picking, the cotton is hauled to the cotton gin as shown in B. This is a machine for separating the seeds from the cotton



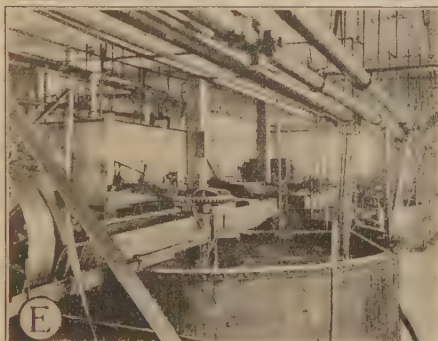
In C the seeds are carefully separated from all foreign matter, such as sticks and pebbles, and then taken to the storehouse

FIG. 161, A, B, and C. The cottonseed oil industry

In D the clean seeds are crushed and heated, then placed in large presses and subjected to great pressure. In this way the oil is squeezed out. The solid matter left (about 20 per cent by weight of the seeds) is a valuable cattle food



The crude oil obtained in D is dark in color and is refined by pouring it into large tanks (E) and treating it with sodium hydroxide and other compounds and finally with a porous clay known as fuller's earth



In F are shown in jar 1 the crude cottonseed oil just as it comes from the seed, in jar 2 the refined oil, and in jar 3 the oil after its treatment with hydrogen (hydrogenated oil)

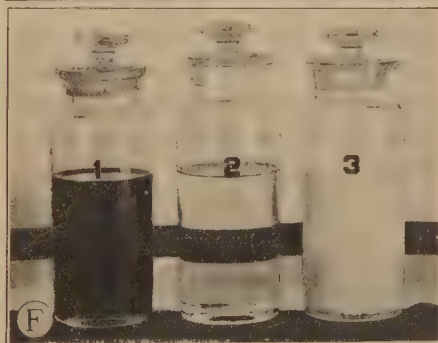


FIG. 161, D, E, and F. The cottonseed oil industry

Butter fat and oleomargarine. While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of a small amount (about 8 per cent) of the fat *butyrin*, which is an ester of butyric acid and has the formula $C_3H_5(C_4H_7O_2)_3$. Oleomargarine differs from butter mainly in the fact that a smaller amount of butyrin is present. It is made from the fats obtained from cattle and hogs. Sometimes cottonseed and coconut oils are also added or are used alone. These fats are churned with milk or mixed with a small amount of butter in order to furnish sufficient butyrin to give the butter flavor.

In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the Federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the Federal tax has been paid.

Proteins. The term *protein* is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms and which constitute the principal part of the tissues of the living cell. The *casein* of milk, *gluten* of flour, and *albumin* of egg will serve as examples of typical protein matter. The proteins all contain nitrogen, carbon, hydrogen, and oxygen, and some contain sulfur and phosphorus in addition.

EXERCISES

1. Name the different kinds of fermentation studied and the changes involved in each.
2. Why does it take so long for a barrel of cider to turn into vinegar?
3. What changes are involved in making vinegar from starch?

4. Distilled vinegar is cheaper than cider vinegar, but it is colorless or nearly so. Sometimes it is colored with caramel to imitate cider vinegar. How could you distinguish between such a vinegar and pure cider vinegar?

5. What effect did the passage of the Prohibition Act have on the production of cream of tartar?

6. For what purpose is oleomargarine artificially colored?

7. For what purpose is butter artificially colored?

8. Why does the Federal government permit the coloring of butter but not of oleomargarine unless a tax is paid?

9. Is it possible by the taste alone to distinguish (a) between refined cottonseed oil and olive oil? (b) between butter and oleomargarine?

10. Give examples of substances that the chemist has changed from being a source of expense to a source of great wealth.

11. Ammonium oxalate is a very common chemical reagent. What is its formula?

12. Magnesium citrate is a common medicine. What is its formula?

13. Ordinary rhubarb used as a food contains the potassium acid salt of oxalic acid. What is its formula?

14. Would cider change into vinegar if all air were excluded?

15. The oils obtained from petroleum (such as coal oil and lubricating oil) are often called *mineral oils* to distinguish them from the animal and vegetable oils described in this chapter. How do these two classes of oils differ in composition?

16. What weight of the alcohol of the druggist is necessary to make 100 kg. of distilled vinegar (contains 4 g. of acetic acid in 100 g. of vinegar)?

CHAPTER XXIX

FOODS

Composition and function of foods. While the compounds present in our foods are very numerous and often exceedingly complex, yet they may all be included under a few general heads; namely, *proteins, fats, carbohydrates, mineral matter, and water*. Since the mineral matter is left as a residue when the food is burned, it is listed as *ash* in reporting the analysis of foods. In addition to the above constituents many foods contain small percentages of substances known as *vitamins*, which are essential to life. The composition of the more common foods is given in the table on page 268.

The function and uses of food are also clearly stated in the chart, on the opposite page, prepared by the United States Department of Agriculture. The facts included in this chart are of great importance and should be carefully studied.

While the different classes of food materials are to a certain extent interchangeable, experiments show that a proper mixture of these materials is essential to health. Of course it is true that one can live for many days on a purely protein diet or on a diet purely of fats and carbohydrates; in fact, persons have been known to live for many days without any food whatever (other than water). In all such cases the body derives the necessary materials from the surplus supply always stored up in the normal body.

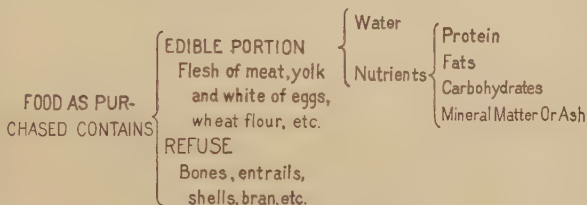
Vitamins. Experiments in recent years have shown that in order for the body to grow and maintain its health there must be present in our foods, in addition to protein, fats,

U.S. Department of Agriculture
Office of Experiment Stations
A. C. True, Director.

Prepared by
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FUNCTIONS AND USES OF FOOD.

CONSTITUENTS OF FOOD.



USE OF FOOD IN THE BODY.

PROTEIN-----	Builds and repairs tissue	{	All serve as fuel to yield energy in the forms of heat and muscular power.
White (albumen) of eggs, curd (casein) of milk, lean meat, gluten of wheat, etc.			
FATS-----	Are stored as fat		
Fat of meat, butter; olive oil, oils of corn and wheat, etc.			
CARBOHYDRATES---	Are transformed into fat		
Sugar, starch, etc.			
MINERAL MATTER OR ASH---	Share in forming bone, assists in digestion, etc.		
Phosphates of lime, potash, soda, etc.			

Food is that which, taken into the body, builds tissue or yields energy.

AVERAGE COMPOSITION OF EDIBLE PORTION OF TYPICAL
FOODS EXPRESSED IN GRAMS PER 100 GRAMS OF FOOD

FOOD	WATER	PROTEIN	FAT	CARBO- HYDRATE	ASH	FUEL VALUE (Cal. per 100 g.)
Almonds	4.8	21.0	54.9	17.3	2.0	647
Apples	84.6	0.4	0.5	14.2	0.3	63
Asparagus	94.0	1.8	0.2	3.3	0.7	22
Bacon (smoked)	20.2	9.9	64.8	—	5.1	623
Bananas	75.3	1.3	0.6	22.0	0.8	99
Beans (dried)	12.6	22.5	1.8	59.6	3.5	345
Beans (string)	89.2	2.3	0.3	7.4	0.8	42
Beef (lean steak)	70.0	21.0	7.9	—	1.1	155
Beef (slightly fat)	73.8	22.1	2.9	—	1.2	115
Beets	87.5	1.6	0.1	9.7	1.1	46
Bread (corn)	38.9	7.9	4.7	46.3	2.2	259
Bread (graham)	35.7	8.9	1.8	52.1	1.5	260
Bread (white)	35.3	9.2	1.3	53.1	1.1	260
Butter	11.0	1.0	85.0	—	3.0	769
Cabbage	91.5	1.6	0.3	5.6	1.0	32
Carrots	88.2	1.1	0.4	9.3	1.0	45
Celery	94.5	1.1	0.1	3.3	1.0	19
Chestnuts	45.0	6.2	5.4	42.1	1.3	242
Chicken	63.7	19.3	16.3	—	1.0	224
Codfish (fresh)	82.6	15.8	0.4	—	1.2	67
Corn (green)	75.4	3.1	1.1	19.7	0.7	101
Dates	13.8	1.9	2.5	70.6	1.2	313
Eggs	73.7	14.8	10.5	—	1.0	154
Figs	18.8	4.3	0.3	74.2	2.4	317
Ham (lean, smoked)	53.5	20.2	20.8	—	5.5	268
Lettuce	94.7	1.2	0.3	2.0	0.9	16
Macaroni	78.4	3.0	1.5	15.8	1.3	89
Milk	87.0	3.3	4.0	5.0	0.7	69
Oatmeal	7.3	16.1	7.2	67.5	1.9	400
Olive oil	—	—	100.0	—	—	900
Oranges	86.9	0.8	0.2	11.6	0.5	51
Peaches	89.4	0.7	0.1	9.4	0.4	41
Peanuts	9.2	25.8	38.6	24.4	2.0	548
Peas (green)	74.6	7.0	0.5	16.9	1.0	100
Plums	78.4	1.0	—	20.1	0.5	84
Potatoes	78.3	2.2	0.1	18.4	1.0	83
Prunes (dried)	22.3	2.1	—	73.3	2.3	302
Raisins	14.6	2.6	3.3	76.1	3.4	345
Rice	12.3	8.0	0.3	79.0	0.4	351
Salmon	64.6	21.2	12.8	—	1.4	200
Spinach	92.3	2.1	0.3	3.2	2.1	24
Strawberries	90.4	1.0	0.6	7.4	0.6	39
Tomatoes	94.3	0.9	0.4	3.9	0.5	23
Turnips	89.6	1.3	0.2	8.1	0.8	40
Wheat flour	11.9	13.3	1.5	72.7	0.6	357

These values are taken from *Bulletin No. 28*, office of Experiment Station, Washington, D. C. The fuel values are obtained from the following formula:

Cal. in 100 g. = $4P + 9F + 4C$, in which P , F , and C represent respectively the number of grams of protein, fat, and carbohydrates in 100 g. of the food.

carbohydrates, and mineral matter, small amounts of certain substances which are known as *vitamins*. But little is known of them beyond their physiological effects. Foods from which they have been extracted, although containing the necessary amounts of protein, carbohydrates, and fats, no longer nourish the body and maintain health. At least three kinds of vitamins are known to exist. The names of these, together with the function of each and some food which is particularly rich in each, are as follows:

1. ***Fat soluble A.*** Promotes growth, keeps the body in good condition, and thus prevents disease in general. Present in milk and butter.

2. ***Water soluble B.*** Prevents the disease known as beri-beri. Present in fresh vegetables and yeast.

3. ***Water soluble C.*** Prevents scurvy. Present in the juices of the tomato, the orange, and the lemon.

All three kinds are abundant in green vegetables such as lettuce and spinach and in milk. Just how these vitamins act to promote growth and prevent disease is not known. It may be that their function is something like that of a catalytic agent, but this is simply a guess.

Energy value of foods. Experiments show that the heat of the body, as well as the energy used in muscular work, results from the oxidation of food materials. The foods, when eaten, undergo complex changes in which the insoluble portions are converted into soluble compounds. These are absorbed into the system and then either undergo oxidation directly or are temporarily built into tissues which later undergo oxidation. In this process most of the carbon is finally changed into carbon dioxide and exhaled from the lungs, while the hydrogen is changed into water. The nitrogen is excreted largely in the form of urea ($\text{CO}(\text{NH}_2)_2$).

Broadly speaking, foods may be regarded as fuel from the oxidation of which in the body the energy necessary for

physical requirements is set free. In the study of foods it is convenient, therefore, to use their *fuel values* (heats of combustion) as a basis of comparison. These values are determined in the calorimeter and expressed in large calories (Cal.), which are 1000 times as large as the small calorie (cal.).

Now experiments show that the body obtains from each of the three classes of foods, when absorbed in the system and oxidized, approximately the following fuel values:

CLASS OF FOODS	CALORIES PER GRAM	CALORIES PER POUND
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

Amount and nature of foods necessary for health. Many studies have been made in order to find out just how much and what kind of food is best adapted for the preservation of health. Evidently many conditions, such as one's age, weight, and occupation and the climate in which one lives, enter into the problem.

Since the fats and carbohydrates have nearly the same function, it is sufficient in stating food requirements for a period of, say, twenty-four hours, to give simply the weight of protein necessary, together with the total fuel value. The difference between the total fuel value and that of the required protein gives the number of calories to be supplied from fats and carbohydrates. Such a mixture of these two food materials is selected so that the fuel value of the mixture, together with the fuel value of the protein, equals the total fuel value required. Different dietary standards have been proposed, but the following (p. 271) given by Atwater are generally accepted. They give the food requirements for a period of twenty-four hours.

CHARACTER OF INDIVIDUAL	PROTEINS REQUIRED	FUEL VALUE REQUIRED
Man with very hard muscular work (wood-chopper, football player)	175 g.	5500 Cal.
Man with moderately active muscular work	125 g.	3400 Cal.
Man with light to moderate muscular work	112 g.	3050 Cal.
Man at sedentary occupation or woman with moderately active work	100 g.	2700 Cal.
Man at rest or woman with light muscular work	90 g.	2450 Cal.
Boy 15 to 16 years	108 g.	3060 Cal.
Boy 13 to 14 years or girl 15 to 16	100 g.	2700 Cal.
Boy 12 to 13 years or girl 14 to 15	87 g.	2380 Cal.
Boy 10 to 11 years or girl 10 to 12	75 g.	2040 Cal.
Boy 6 to 9 years	62 g.	1700 Cal.

In selecting our foods, however, it is essential not only that we secure the proper proportion of protein, fats, carbohydrates, and mineral matter, but we must also consider whether the foods selected contain these ingredients in a palatable and digestible condition. Especially must we make such a selection as will furnish us with the necessary vitamins; in other words, *we must take into consideration quality as well as quantity of food*. For these reasons some foods, such as milk, may not seem to rank high as an economical food considered simply from its content of fat, carbohydrate, and protein; yet when we take into account the character of these constituents present in milk and especially its vitamin and mineral content, its effect in maintaining health as well as in nourishing the body makes it one of our most valuable foods.

Laws of the conservation of energy and matter in the human body. In studying the food requirements of the human body many experiments have been made to find out whether or not the laws holding good in the inanimate world (namely, the laws of the conservation of matter and energy) hold good also in the processes taking place in the living organism. So far as the law of

conservation of matter is concerned, the question can be answered by carefully comparing the air breathed and the food eaten (*intake*) with the products stored up in the body and with the products exhaled or excreted (*output*).

In order to measure the energy changes, however, one must be able to determine the amount of heat evolved. This is done by means of the *respiration calorimeter*. This is a chamber large

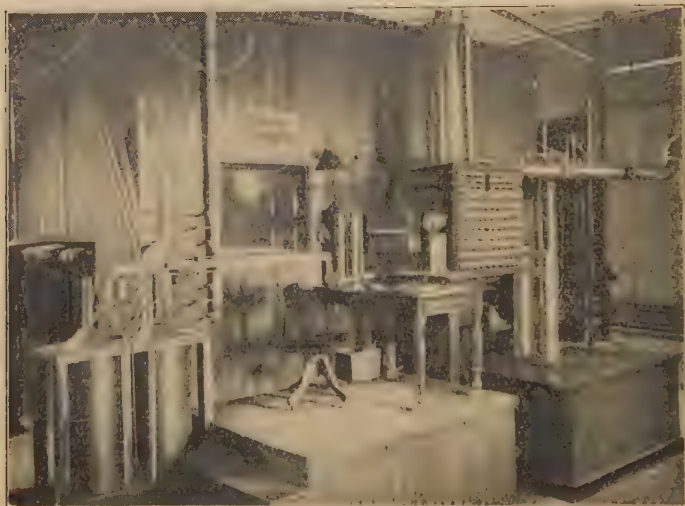


FIG. 162. Exterior of a respiration calorimeter

enough to enable one to live in it and constructed with double walls of nonconducting material so as to prevent loss of heat through radiation; in fact, it is a large calorimeter (Fig. 126).

With the necessary precautions it is possible in this way to measure the heat generated in the body of a person living within the calorimeter. The experiments show that the changes in matter and energy which take place in the human body are in accord with the laws of the conservation of matter and energy.

Fig. 162 shows the exterior of a respiration calorimeter, also the apparatus for analyzing the air admitted and measuring the heat evolved by the person in the calorimeter.

Cost of food as related to its nutritive value. It will be noted that the food requirements for the body are stated simply in terms of protein, carbohydrates, and fats, but such a selection of these must be made as will contain the necessary vitamins. It is very evident that the cost of, say 100 g., of protein will vary according to the source of the protein.

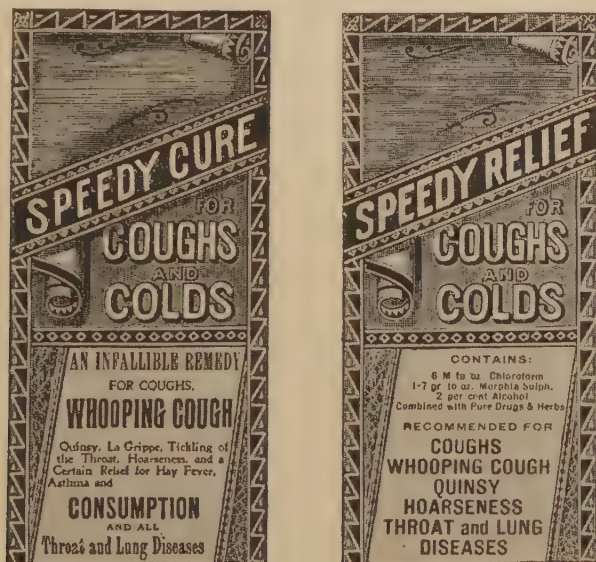


FIG. 163. The label on a well-known patent medicine before and after the passage of the Pure Food and Drugs Act

For example, protein obtained in the form of tenderloin steak will cost much more than an equal weight of protein obtained from dried beans. Again, there is as much nutriment in 1 lb. of wheat flour as in $3\frac{1}{2}$ qt. of oysters, although the latter is far more expensive. By finding the selling prices of the various foods given in the table on page 268, one can easily determine the relative cost of various food materials obtained from different sources.

Pure Food and Drugs Act. In 1906 the Federal congress passed what is known as the Pure Food and Drugs Act. This fixes the standard of various foods and drugs, and prescribes that all labels must tell the truth and must state the presence of any dangerous or habit-forming drugs. The effect of the act may be seen by a study of Fig. 163, which shows the label used on a well-known patent medicine before the act was passed and also how it had to be modified to meet the requirements of the act.

EXERCISES

1. Is the ash obtained in burning a food necessarily present in that form?
2. Why do different nations use different kinds of foods?
3. Why do we enjoy certain kinds of foods more in winter than in summer?
4. Mention foods that are rich in water; in protein; in fats; in carbohydrates.
5. From the current prices of foods work out a list of the most economical ones to use as a source of protein; of carbohydrates; of fats.
6. If one wishes to grow thin, what kinds of foods ought to be avoided?
7. In selecting a proper diet what factors must we take into consideration?

CHAPTER XXX

THE PHOSPHORUS FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Phosphorus	P	31.04	1.83	44°
Arsenic	As	74.96	5.73	—
Antimony	Sb	120.2	6.70	630°
Bismuth	Bi	208.	9.80	271°

The family. The elements constituting this family belong in the group with nitrogen and therefore resemble it in a general way. They exhibit a regular gradation of properties, as is shown in the above table.

PHOSPHORUS

Properties. We commonly associate the element phosphorus with matches and with bones, for it is well known that it is the substance used to make matches inflammable and that its compounds constitute the principal mineral constituents of bones. The free element is obtained in two chief forms, known as white (or yellow) phosphorus and red phosphorus.

White phosphorus (yellow phosphorus) is a nearly colorless, translucent, waxy solid which melts at 44°. It is sold in the form of sticks (Fig. 164) and is the common form of phosphorus. *Red phosphorus*, on the other hand, is a dark-red powder.

The two allotropic forms of phosphorus differ widely in properties. Thus the white form is very poisonous, is soluble in carbon disulfide, and ignites so readily that it must be kept under water

and handled with the greatest care. It is easily cut into pieces, *but this must always be done under water* to avoid ignition. Red phosphorus, on the other hand, does not ignite easily, is not soluble in carbon disulfide, is not poisonous, and has a high melting point. White phosphorus is formed when any form of the element is distilled and its vapor condensed in cold water. On standing at ordinary temperatures it slowly changes into the red variety; at higher temperatures the change is much more rapid.



FIG. 164. Phosphorus and some of its most common compounds

History and occurrence. Phosphorus has long been known, having been discovered in 1669 by the alchemist Brand while searching for the philosopher's stone. It occurs almost entirely in various mineral forms of calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). *Phosphorite* is the most abundant of these minerals, while *apatite* consists of calcium phosphate, together with calcium fluoride or chloride. Calcium phosphate is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

Preparation. The element is prepared by heating a mixture of calcium phosphate, sand, and carbon in an electric furnace. Phosphorus is liberated as a vapor, and this is condensed under cold water and cast into stick form as the white variety.

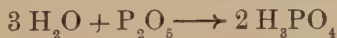
Chemical conduct. The most striking property of white phosphorus is its affinity for oxygen. When exposed to cool air it slowly combines with oxygen, and in so doing gives out a pale light, or *phosphorescence*, which can be seen only in a dark place; hence the word *phosphorus*, which means "light producer." The heat of the room may raise the temperature of phosphorus to the kindling point, when it burns with a sputtering flame, giving off dense fumes of oxide of phosphorus. It burns with dazzling brilliancy in oxygen and combines directly with many other elements. On account of its great attraction for oxygen it is preserved under water.

Compounds. While phosphorus forms many compounds, only a few of them are of common importance.

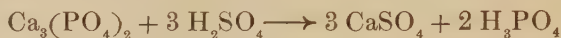
1. **Oxides.** Phosphorus forms two well-known oxides—the trioxide (P_2O_3) and the pentoxide (P_2O_5), sometimes called *phosphoric anhydride*. The pentoxide is much the better known of the two. It is formed when phosphorus burns in oxygen or air and is a snow-white, voluminous powder (Fig. 164) whose *most marked property is its great attraction for water*. It has no chemical action upon most gases, so that they can be very thoroughly dried by being passed through properly arranged vessels containing phosphorus pentoxide.

2. **Sulfide.** When phosphorus and sulfur are brought together under certain conditions, they combine to form *phosphorus sesquisulfide* (P_4S_3). This is a dark-colored solid and is largely used in making matches.

3. **Acids.** Phosphorus forms a number of acids, but the only very important one is phosphoric acid (H_3PO_4). The pure compound forms large, colorless crystals; ordinarily the acid contains a little water, and it then forms a thick, sirupy liquid (Fig. 164). If a solution of the pure acid is desired it is prepared by burning phosphorus and adding water to the pentoxide so formed:



The ordinary solution, however, is prepared by treating calcium phosphate with sulfuric acid:



The calcium sulfate (CaSO_4) formed is nearly insoluble and can be separated from the phosphoric acid by filtration. Being a *tribasic* acid, it forms acid salts as well as normal salts. Thus the following sodium salts are known:

NaH_2PO_4		primary, or monosodium-hydrogen phosphate
Na_2HPO_4		secondary, or disodium-hydrogen phosphate
Na_3PO_4		tertiary, or normal sodium phosphate

Uses. Because of its poisonous properties white phosphorus is used as a rat poison. It is also used in making pure phosphoric acid and for minor purposes in chemical laboratories. During the World War large amounts were used in generating smoke clouds (P_2O_5) for concealing troops and ships (Fig. 165). The incendiary bullets which proved so disastrous to the Zeppelins during the war contained free phosphorus. When fired, the phosphorus was ignited by the friction of the air, and, on hitting a balloon or Zeppelin, set fire to the hydrogen with which they were filled. *The chief use of phosphorus, however, is in the making of matches.*

Matches. Friction matches containing phosphorus first came into use in 1827, and at present two general varieties are in common use. The more common variety which will ignite when rubbed against any rough surface is made by dipping the match stick first into some inflammable substance, such as melted paraffin, and afterwards into a paste consisting of (1) phosphorus sesquisulfide, P_4S_3 ; (2) some oxidizing substance, such as manganese dioxide, red lead, or potassium chlorate; and (3) a binding material, such as glue or dextrin. On friction the phosphorus is ignited, the combustion being supported by the oxidizing agent and communicated to the wood by the burning paraffin. In sulfur matches the paraffin is replaced by sulfur.

In the *safety* match red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface.



FIG. 165. The use of phosphorus in the World War for concealing troops
Often when troops were ready for an attack, shells filled with phosphorus were fired. When these exploded, the phosphorus burned, forming dense clouds of the oxide which entirely concealed the troops

Constant working with white phosphorus frequently results in dreadful diseases of the bones of the face, while many disastrous fires are caused by accidental ignition of matches containing it. On this account the manufacture and use of such matches is prohibited by law in many countries. The congress of the United States in 1913 accomplished the same end by imposing a prohibitive tax upon white-phosphorus matches.

Phosphates. The phosphates form an important class of salts. The most important phosphate is calcium phosphate, which is mined in enormous quantities for use as a fertilizer.

ARSENIC

General discussion. When we hear the word *arsenic* we are apt to think of a poisonous substance because it is well known that materials containing arsenic are poisonous in character. The element itself is a steel-gray solid and occurs in nature combined with sulfur. Small amounts of the element combined with metals are associated with copper ores. In

the separation of copper from these ores the arsenic is obtained as a by-product in the form of the oxide As_2O_3 . The element can be obtained from this by heating with carbon:



Arsenic burns when heated in air, forming the oxide As_2O_3 .

Compounds. When hydrogen is generated in contact with arsenic or its compounds a *very poisonous*, colorless gas known as *arsine* (AsH_3) is generated. The most common compound of arsenic is the oxide As_2O_3 ,

known as arsenic trioxide or *arsenious oxide*, or often as *white arsenic*. It is a rather heavy white solid, obtained either as a crystalline powder or in lumps resembling porcelain in appearance (Fig. 166). It is very poisonous, from 0.2 to 0.3 g. being a fatal dose. Arsenic also forms a number of acids, the most important of which are *arsenious acid* (H_3AsO_3) and *arsenic acid* (H_3AsO_4). Some of the salts of these acids are of considerable importance.

Uses. Arsenic in the free state is little used. About 0.5 per cent of arsenic is added to lead used in making shot, since this makes the lead harder. The compound of arsenic most



FIG. 166. The two common forms of arsenic trioxide

widely used is the oxide As_2O_3 . This is used in preparing all the other compounds of arsenic. It is also used in making glass and as a preservative in mounting the skins of birds and animals. Its greatest use is in the preparation of insecticides for spraying trees and killing insects on stock.

Arsenic insecticides. Several compounds of arsenic have important uses as insecticides. *Paris green* and *Scheele's green* are complex salts made by treating solutions of copper salts with arsenious oxide. The commercial *lead arsenate* so widely used in connection with lime-sulfur sprays (p. 185) is chiefly $\text{Pb}_3(\text{AsO}_4)_2$.

ANTIMONY

General discussion. Antimony is a silverlike, brittle solid a little lighter than iron. It melts at 630° and expands somewhat on solidifying. It is found in nature chiefly in the form of *stibnite* (Sb_2S_3), from which it is obtained by heating with iron:

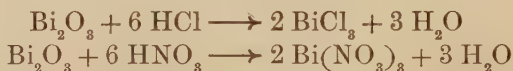


It forms a number of compounds which resemble the corresponding compounds of arsenic in composition and properties. Its chief use is in making *alloys* (p. 282), especially the one known as *Babbitt metal*.

BISMUTH

General. Bismuth resembles antimony in appearance except that it has a slightly rosy tint. It is a little heavier than iron, but melts at a low temperature (271°). It occurs in nature chiefly in the free state, and our supply comes largely from Bolivia. Like antimony, its chief use is in the making of alloys. The element differs from the other elements of the phosphorus family in that it has practically no acid properties, but forms salts like the metals. Sulfuric and nitric

acids dissolve it just as they do copper. When heated in the air it burns, forming the oxide Bi_2O_3 , and this dissolves in acids, forming salts:



These salts are colorless, crystalline solids.

Action of water on bismuth salts. The salts of bismuth react with water as shown in the following equations:



The compound BiOCl , known as *bismuth oxychloride*, as well as the corresponding *bismuth oxynitrate*, BiONO_3 , are white solids, the latter being often used in medicine.

ALLOYS

Bismuth and antimony and many of the metals when melted together thoroughly intermix, and on cooling form a uniform metal-like substance called an *alloy*. Not all metals will mix in this way, and in some cases definite chemical compounds are formed and separate out as the mixture solidifies, thus destroying the uniform quality of the alloy. In general, the melting point of the alloy is below the average of the melting points of its constituents.

Both antimony and bismuth alloy readily with many of the metals. The alloys so formed are heavy, are easily melted, do not oxidize easily nor act upon water, and, in general, are well adapted to many technical uses. The manufacture of alloys constitutes the chief use of these two elements.

Antimony imparts to its alloys the property of expanding slightly in solidification, which renders them especially useful in type founding, where fine lines are to be reproduced on

a cast. *Type metal* consists of antimony, lead, and tin. *Babbitt metal*, largely used in the construction of certain parts of machinery, contains the same metals in a different proportion, together with a small percentage of copper.

Bismuth is particularly valuable in the production of very low-melting alloys. For example, *Wood's metal*, consisting of bismuth, lead, tin, and cadmium, melts at 60.5° . The low melting point of such alloys is turned to practical account

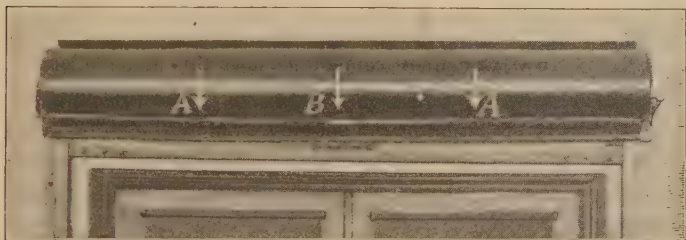


FIG. 167. An automatic fire curtain above a door

in making safety plugs in boilers, automatic fire curtains and automatic water sprinklers in buildings, and in many similar devices.

Fig. 167 shows a fire curtain, which is held in place by two wires *A*, *A*, joined at *B* by a bismuth alloy. In case of fire the alloy melts and the wires holding the curtain up are thereby released and the curtain drops, covering the door.

EXERCISES

1. What elements have we studied that occur in allotropic forms?
2. What substances have we studied that are used as insecticides?
3. Nitrogen occurs in the same group in the periodic table as the phosphorus family. Can you point out any similarity in chemical conduct?
4. Approximately, what weight of phosphorus is present in your body (p. 10)? In what form is it present?

5. By far the greater part of the phosphorus used in the United States is made at Niagara Falls. What is the advantage of this locality for the production of phosphorus?

6. In what connection has phosphorus been referred to in an earlier chapter?

7. How does an automatic water sprinkler in a building operate to extinguish fires?

8. In the equation on page 280 what does the character As_4 indicate?

9. Write the formula and give the name (*a*) of the sodium salt of arsenious acid; (*b*) of arsenic acid.

10. Phosphorus pentoxide combines with water to form phosphoric acid (p. 277). To what class of compounds does this oxide belong?

11. Why does cutting a piece of phosphorus cause it to ignite?

12. What is the function of the potassium chlorate used in ordinary matches?

13. 100 kg. of pure calcium phosphate would yield what weight of phosphorus?

14. What weight of phosphoric acid could be prepared by burning phosphorus in air and adding water to the product? (*Suggestion.* 1 atom of phosphorus forms 1 molecule of phosphoric acid.)

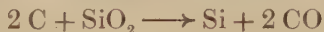
15. What weight of antimony could be prepared from 1 ton of stibnite?

CHAPTER XXXI

SILICON AND BORON

SILICON

General. Just as carbon is the most essential element present in living matter (plants and animals), so silicon is the most essential element present in the compounds that constitute the soils and the rocks that make up the earth's crust. It is therefore very abundant, being next to oxygen in this respect. Notwithstanding this fact it is not so familiar as many other elements of rarer occurrence. This is because it never occurs native. It can be prepared by heating a mixture of sand (SiO_2) and carbon in an electric furnace:



It is a bright, metallic, brittle solid and is used largely for making certain varieties of iron and iron alloys.

Silicon occurs in nature chiefly in the form of silicon dioxide (*silica*), SiO_2 , or in the form of salts of silicic acids (*silicates*). These compounds constitute almost all the common rocks except limestone. Plants absorb small amounts of silica from the soil, and it is also found in minute quantities in animal organisms, especially in hair, claws, and horns.

Silicides; carborundum. As the name indicates, *silicides* are compounds consisting of silicon and some one other element. They are very stable at high temperatures and are usually made by heating the appropriate substances in an electric furnace.

The most important silicide is *carborundum*, which is a silicide of carbon of the formula CSi . When carbon is heated with sand in an electric furnace, the element is first liberated as shown under the preparation of silicon. Under proper conditions the silicon then combines with excess of carbon to form CSi , and it is in this way that carborundum is prepared.

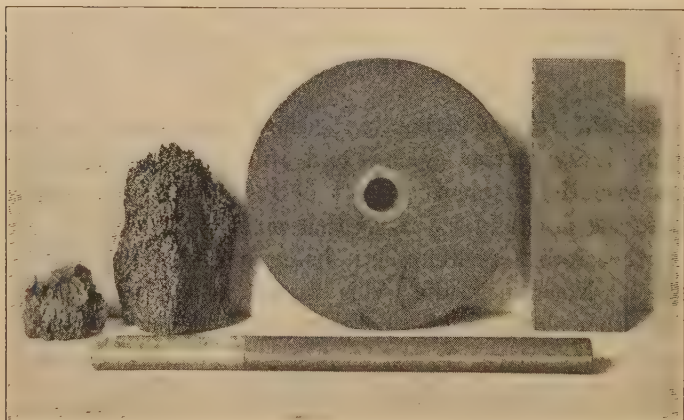


FIG. 168. Crystals of carborundum and abrasive utensils made of carborundum

Large quantities of this product are made at Niagara Falls. It can be obtained as perfectly colorless crystals, but as made commercially the crystals have a beautiful purplish-black color, the color being imparted to it by the presence of small amounts of certain other elements, chiefly iron. Carborundum is very hard, being surpassed in this property only by the diamond and one or two rare compounds. It is this property which makes it so valuable. It is used as an abrasive; that is, as a material for grinding and polishing very hard substances. Fig. 168 shows two samples of the crystalline material, as well as whetstones and a grinding-wheel prepared from carborundum.

Manufacture of carborundum. The materials used in making carborundum are carbon, sand, common salt, and sawdust. The salt assists in the reaction, while the sawdust burns away, leaving the mass porous and thus allowing the escape of gases. The mixture of these materials is heated in a large resistance furnace similar to the one employed in the manufacture of graphite (p. 104). Fig. 169 shows a furnace in operation. The carbon monoxide formed escapes and burns as shown in the figure.

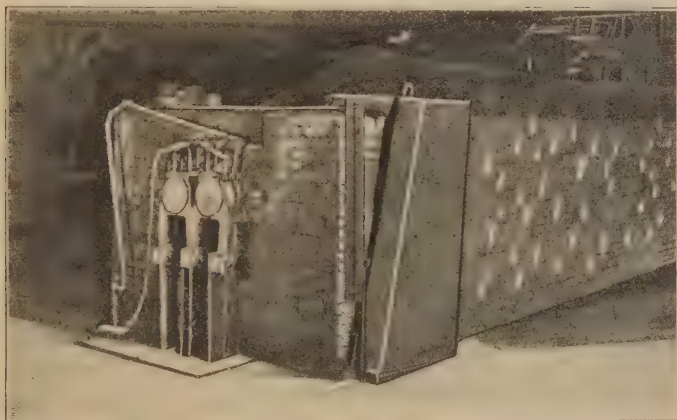


FIG. 169. A carborundum furnace in operation

Silicon dioxide (silica) (SiO_2). This substance is found in a great variety of forms in nature, both in the amorphous and in the crystalline condition. In the form of *quartz* (Fig. 170) it is found in beautifully formed six-sided prisms, sometimes of great size. When pure it is perfectly transparent and colorless. Some colored varieties are given special names, as *amethyst* (violet), *rose quartz* (pale pink), *smoky* or *milky quartz* (colored and opaque). Other varieties of silicon dioxide, some of which also contain water, are *chalcedony*, *onyx*, *jasper*, *opal*, *agate*, and *flint*. *Sand* and *sandstone* are largely silicon dioxide.

The skeletons of certain microorganisms (infusoria) are composed of nearly pure silica. In some localities these have

accumulated in immense deposits, forming a very fine and sharp sand called *infusorial earth*. This material is often used as a scouring-powder, especially in scouring-soaps.

Properties. As obtained by chemical processes, silicon dioxide is an amorphous white powder. In the crystallized state it is very hard and has a density of 2.6. Pure silica begins to soften at about 1600°, and somewhat above this temperature



FIG. 170. A cluster of quartz crystals

it can be drawn out into threads and blown like glass into tubes and small vessels. These articles are attacked by comparatively few ordinary reagents and do not expand or contract to any appreciable extent with even very great changes in temperature. On this account a quartz vessel can be heated red hot and plunged into cold

water without cracking. Unfortunately they are quite expensive, but their use is steadily increasing. Fig. 171 shows a quartz crucible and quartz tubes on a wire triangle used to support the crucible when heated. Silicon dioxide is very inactive, but is readily attacked by hydrofluoric acid (p. 205). When heated to high temperatures with compounds of the metals, especially the carbonates and sulfates, *silicates* (salts of silicic acids) are formed as follows:

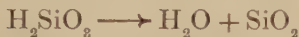


It is this reaction which is used in making glass.

Silicic acids. Silicon forms two simple acids, *orthosilicic acid* (H_4SiO_4) and *metasilicic acid* (H_2SiO_3). Orthosilicic acid is formed as a jellylike mass when orthosilicates are treated with strong acids. If one attempts to dry this acid it loses water, passing into metasilicic acid (common silicic acid):

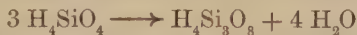


Metasilicic acid, when heated, breaks up into silica and water, thus:



Salts of silicic acids; silicates. A number of salts of the orthosilicic and metasilicic acids occur in nature. Thus, *mica* (KAlSiO_4) is a salt of orthosilicic acid.

Polysilicic acids. Silicon has the power to form a great many complex acids which may be regarded as derived from the union of several molecules of orthosilicic acid, with the loss of water. These are called *polysilicic acids*. For example, we have



Salts of these acids make up the great bulk of the earth's crust. *Feldspar*, for example, has the formula KAlSi_3O_8 and is a salt of the acid $\text{H}_4\text{Si}_3\text{O}_8$, whose formation is represented in the equation above. *Kaolin*, or pure clay, has the formula $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ or, as commonly written, $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$. *Granite* is composed of crystals of feldspar and mica cemented together with amorphous silica.

Water glass. Sodium silicate and potassium silicate differ from the silicates of the other metals in that they are soluble in water. The common *water glass* is a solution of sodium silicate. It is a thick, sticky liquid made by fusing sand with

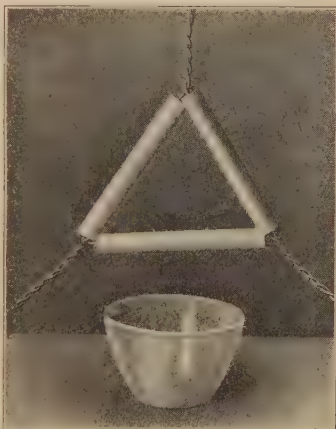


FIG. 171. A crucible and a triangle made from quartz

sodium carbonate. It is used for the purpose of giving a glazed waterproof surface to porous materials, such as wood, stone, and plaster; to render curtains noninflammable; as a glue for mending glass and pottery and for making strawboard boxes; and as an ingredient of cheap soaps.

Its property of closing pores is turned to account in preserving eggs for winter use. The eggs are packed in crocks and then covered with a liquid made by adding 1 volume of commercial water glass to 10 volumes of water. Over the liquid is then poured a little melted paraffin, which soon hardens and excludes the air. Fresh eggs can easily be preserved for six months in this way.

BORON

General discussion. Boron is a gray solid, difficult to prepare, and in the free state but little used. It occurs in nature in the form of the mineral *colemanite* ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) (Fig. 172). This is mined in southern California and is the source of the compounds of boron prepared for commercial uses.

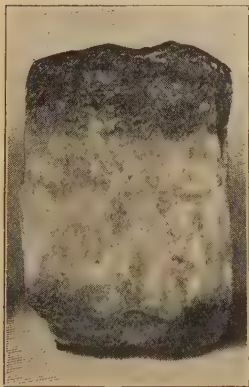


FIG. 172. A specimen of colemanite, the mineral from which borax is made

Compounds. The most important compounds of boron are the following:

Boric acid (H_3BO_3). This is a white solid, slippery to the touch. It is a mild antiseptic and is used in medicines.

Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$). If we add sodium hydroxide to boric acid we do not get a salt of the simple acid, but one that has the formula $\text{Na}_2\text{B}_4\text{O}_7$ and is called *sodium tetraborate*.

When this is crystallized from water at ordinary temperatures the crystals are composed of this salt, together with water, and have the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. This compound is called *borax*.

Water of crystallization ; hydrates. Many salts when crystallized from water are found to have formed compounds with the water, and if the crystals are heated the water can be driven off as steam. Such salts are called *hydrates*, and the water is sometimes referred to as *water of crystallization* or *water of hydration*—though many crystals do not contain water. A salt which has crystallized without combining with water is said to be *anhydrous*. In the formula of a hydrate it is customary to write the formula of the salt and the water separately with a period between. Thus the formula of borax is written $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. This formula expresses the fact that in the crystals each molecule of sodium tetraborate is combined with 10 molecules of water.

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$). Borax (Fig. 173) is the most important compound of boron, many thousands of tons of it being made annually from colemanite. It is a white solid and crystallizes in large crystals. When borax is heated, it swells up in a sort of froth, owing to the escape of steam, and this soon melts to a clear glass. The glass has the property of easily dissolving many metallic oxides, and this fact is turned to account in working with metals. When two pieces of metal are to be joined by melting them together or by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint to clean the metal and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the borax glass with characteristic



FIG. 173. Large crystals of borax

tints. On this account little beads of borax are used in testing for the presence of such metals.

Borax is extensively used as a constituent of enamels and glazes for both metal ware and pottery. It is often used in our homes to soften hard water, as a mild alkali (like soap), and as an antiseptic.

EXERCISES

1. What substances have we studied that are prepared (a) by heating in an electric furnace? (b) by passing a current of electricity through a liquid?

2. How could you distinguish between a quartz crystal and a diamond?

3. How do you account for the fact that some samples of sand are white and others colored?

4. What is the formula of the acid of which kaolin is the salt?

5. What is the advantage and the disadvantage of quartz glass?

6. To what class of substances does granite belong?

7. Is the water of hydration present in a compound in the form of water or is the water in a combined state?

8. Could you tell from the appearance of a compound whether it contained water of hydration?

9. What is the weight of the water of crystallization in 1 ton of borax?

10. State the chemical composition of each of the following substances: graphite, boneblack, muriatic acid, caustic soda, kaolin, sand, flint, opal. $\checkmark$ $\text{Ca}_3(\text{PO}_4)_2$ 14 ex. $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$

11. Give another name for each of the following: laughing gas, oil of vitriol, cane sugar, cream of tartar, white arsenic.

CHAPTER XXXII

COLLOIDS — THE CHEMISTRY OF VERY SMALL PARTICLES

Introduction. We all know that coarse sand shaken up with water quickly settles when we stop shaking the mixture. The finer the sand the slower it will settle. If we powder it fine enough and then stir it into water, it will not settle at all, for the particles will be so small that they will be kept in constant motion by collision with the molecules of the water. If we could powder the sand into individual molecules and stir them into water, we would have a true solution.

In this chapter we shall be interested in these very fine particles that are too small to settle, cannot be seen directly by even the best of microscopes, and yet consist of many thousands of molecules. Such particles suspended in a liquid are called *colloidal dispersions* or *colloids*, and matter in this condition is said to be in the *colloidal state*.

The air in a quiet room contains many particles of colloidal size that are too small to be seen as objects by a microscope. But if the room is dark and a beam of sunshine enters through a small hole, these minute particles can be seen as bright, flashing points or motes dancing in the sunbeam. In like manner a colloidal suspension in a liquid that appears perfectly clear to the eye is seen to be full of moving particles when a strong beam of light shines through the liquid (Fig. 174).

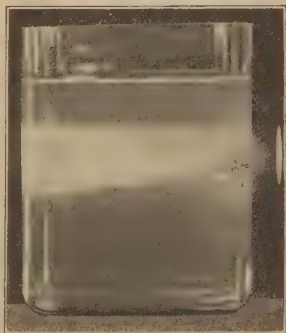


FIG. 174. A beam of light shining through a colloidal solution

How colloids are made. There are two general plans for making colloids, each of which may be modified in many details:

1. An insoluble solid may be actually powdered to the necessary fineness and then stirred into the liquid (usually water). For example, we may prepare a colloidal dispersion of gold, silver, or platinum by establishing an electric arc between wires of the metal immersed in water. The current tears off minute particles as a kind of smoke and disperses them through the water (Fig. 175). Almost any sample of sand or ocean water shows traces of gold probably powdered to colloidal size by the natural grinding processes of nature.

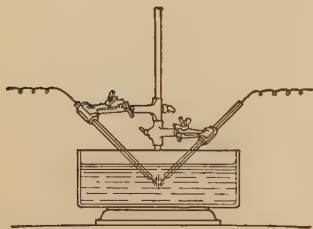


FIG. 175. The preparation of metallic colloids by sparking under water

2. We may bring about a reaction that ordinarily produces a precipitate, but under conditions such that the minute particles formed at first fail to gather together into particles large enough to settle as a precipitate. For example, we may add acid to a dilute solution of the salt known as sodium thiosulfate. No immediate precipitate of sulfur forms, but colloidal sulfur is present, as is evident from the white color. After a time some sulfur may precipitate, but most of it remains in suspension.

Properties of colloids. Most of the interesting properties of colloids are due to the size of the particles rather than to the kind of matter of which they are made.

1. All colloidal particles are charged electrically, some kinds positively and some negatively, and in an electrical field they act like the ions of a salt.

2. Many colloids are highly colored, but the color gives us little clue as to what is present. Thus colloidal gold may

be red, blue, green, or violet, depending upon the size and uniformity of the particles. A little ferric chloride added to boiling water gives a deep-red colloidal iron oxide. It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass makes the intensely red glass of the automobile tail-light. Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way. The blue of the sky and of deep mountain lakes is probably due to colloidal dust in the air and the water.

3. Since the colloidal particles are exceedingly small they cannot be filtered out by any ordinary filter.

4. Many colloids have the property of adsorbing dissolved material from solutions. Thus ammonia is easily adsorbed by various colloids.

Coagulation of colloids. It often happens that a colloidal dispersion is objectionable, and we want to remove it or recover the colloidal material. We must then change the electrical or chemical conditions so that the very small particles will grow together into large clumps that will precipitate. We have found a number of ways to accomplish this:

1. A given colloid is apt to remain suspended in an alkaline solution but to be precipitated in an acid solution; or it may be just the reverse. So the addition of a little acid or alkali is apt to cause the colloid to precipitate, or *coagulate*, as it is called.

Thus casein, an important colloid in milk, coagulates to a curd when the milk becomes sour or acid in reaction. Rubber is coagulated from the sap of rubber trees by the addition of acetic acid. If we try to prepare antimony sulfide in alkaline solution by bringing together hydrogen sulfide and a salt of antimony, we get only a deep-red colloidal dispersion, but if we add acid we get a brick-red precipitate. On the other hand, many metallic oxides are precipitated by alkalies.

2. Sometimes a concentrated salt solution will coagulate a colloid. Thus most river water carries much colloidal clay and organic matter. When it reaches the salt water of the ocean this matter is precipitated and builds up the great river deltas such as those of the Mississippi or the Nile. In every soap factory colloidal soap is separated from its solutions by the addition of common salt.

3. We have seen that all colloids are electrically charged. It has been found that when two colloids of opposite charge are brought together, they mutually precipitate each other. Thus the negative colloids of river water are precipitated by the positive colloids supplied by alum or iron salts in ordinary water purification. The processes of dyeing and tanning depend upon this same principle.

Dispersal of colloids. It frequently happens that in many industrial operations we want to preserve the colloidal state or bring a colloidal precipitate once more into dispersed condition. For many purposes the colloidal suspension of an insoluble solid is just as good as a true solution. We can sometimes use the original methods for preparing a colloid. Thus, by a process similar to grinding, graphite may be suspended in oil or water to make a very effective lubricant for machinery (oil dag and water dag). We may reverse the acidity or alkalinity that caused the coagulation. Thus, antimony sulfide precipitated in acid solution may be dispersed again in an alkaline medium. We may filter the precipitate from the salt solution that produced precipitation and disperse it once more in pure water.

If we bring together two colloids of the same electrical sign they tend each to hold the other in the colloidal state. Thus, we add gum arabic to some kinds of inks to hold the black ink material in suspension. This is the chief reason for adding gums, dextrin, starch, and similar materials to many industrial and medicinal preparations.

Colloids and crystallization. It is an interesting fact that the presence of a colloid often tends to prevent distinct crystallization or at least to make the crystals very small and soft. Hence we put colloidal gelatin into ice cream, and gelatin, starch, dextrin, and similar materials in many candies and in electrolytic baths during electroplating, for in these processes we wish to avoid large or hard crystals. The colloidal materials in honey keep the concentrated sugar solution from crystallizing.

Emulsions. If we pour two liquids together that do not mix, like oil and water, and shake the mixture violently, we get a milky-looking fluid called an *emulsion*. This consists of very minute drops of the one liquid dispersed through the other. If we let the emulsion of oil in water stand, it will very soon separate into the original liquids from which it was made. To make an emulsion of any kind permanent we must add a third colloidal substance insoluble in both of the liquids. This is called the *emulsifying agent* (Fig. 176). It seems to form a little skin over the surface of the drops and pre-



FIG. 176. Emulsions

When oil and water are shaken together, the oil soon separates on standing (A); if a little soap is added to the oil and water, and the mixture shaken, the emulsion becomes more permanent (B)

vents them from running together into big ones. Milk is an emulsion of butter fat in water, with casein as the emulsifying agent. When the milk turns sour and the casein is coagulated, the butter fat is easily collected into large lumps of butter. Most of our common disinfectants and sheep dips owe their properties to cresol emulsified in water, with a small percentage of soap as the emulsifying agent. In mayonnaise,

olive oil is emulsified in water (usually with a little vinegar added) by the colloidal yolk of egg, forming a stiff almost jellylike product. The fluids that form the webs of spiders and silkworms are secreted as emulsions that almost at once dry to form very fine filaments.

Jellies. Sometimes a colloidal substance tends to form very thin films rather than particles or filaments, and these films



FIG. 177. View of a factory showing the effect of the Cottrell method for abating dust and smoke

may form in such a way as to inclose the liquid much as the walls of the honeycomb inclose the honey or the pores of a sponge hold water. When this happens the whole dispersion is likely to set to a more or less firm form called a *jelly* or a *gel*. Thus, if we add acid to a solution of sodium silicate the dilute dispersion of silicic acid soon sets to a firm jelly. Casein sets to a jelly when coagulated (Fig. 144). In fruit jellies it is a constituent of the unripe fruit called *pectin* that serves to form the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form, but when dissolved in hot water and cooled a jelly is once more obtained. Soap is a partially dried jelly, and many minerals such as

agate, flint, and opal are dry jellies. Photographic films and many high explosives are jellies. Almost any sparingly soluble substance that does not crystallize too readily may be obtained in the form of a jelly. The so-called *solidified alcohol*, used largely at the present time, consists of a porous soap (Chapter XXXV) and alcohol, the soap acting as a sort of sponge to hold the alcohol. As yet we do not understand the conditions that lead to the formation of these jellies, and we obtain them largely by accident or by a cut-and-try process.

Smokes. Evidently we may have very fine particles suspended in the air rather than in water, and such a suspension is a *smoke*. It is often very hard to condense the particles of a smoke into solid form, and this fact is of enormous industrial importance. Many precious materials literally "go up in smoke" from the stacks of smelters; much zinc is lost as a smoke of zinc oxide in brass foundries; valuable potassium compounds are lost in the smoke of cement burners; and ordinary carbon smoke causes great losses to the individual, but profit to the laundries.

All these smoke particles are electrically charged, and the American chemist Cottrell has devised a most effective process for the recovery of smoke particles by causing the smoke to move past metal plates and points charged electrically. The smoke particles lose their charge and then coagulate much as a precipitate and settle on the sides of the chimney (Fig. 177). The tails of comets are largely made up of particles of colloidal size.

Fogs and foams. Fogs consist of very fine droplets of liquid (usually water) suspended in air, so that they correspond to *emulsions*. Foams are gas bubbles dispersed through a liquid. Sometimes these minute gas bubbles are dispersed through what we should usually consider a solid, and often give to it a pure-white color. Many white flowers, like lilies, owe their whiteness to dispersed gas bubbles, and it appears that white hair is also due to air bubbles in the hair, though no one knows why age or worry should affect the hair in such a way.

EXERCISES

1. Keeping the kinetic theory in mind (p. 47), explain why large particles suspended in a liquid will settle and very small ones will not.
2. (a) What is the difference between saying that a solution is *clear* and that it is *colorless*? (b) Are colloid suspensions ever clear? (c) Are they colorless?
3. The famous Hope diamond is very blue in color. Would a chemical analysis necessarily show the presence of a color pigment?
4. The white of an egg is a typical colloid. In what way is it often coagulated? Can it be restored to the colloidal state?
5. After oil is used in machinery it gets very black (as in the crank case of an automobile), yet very little of the color is removed by ordinary filtration or settling. How do you account for this fact?
6. Why should a fine suspension be as good as a true solution for many purposes?
7. Many salves and ointments are made by rubbing an oil or a soft fat with some other material. How would you classify these preparations?
8. It is difficult to make a good jelly from ripe fruit. Can you suggest a reason for this?
9. There is often enough sugar in a good fruit jelly to make a supersaturated solution. Why does it not more often crystallize out or "sugar"?
10. Fertile soils are essentially a kind of colloid jelly, made up of clay and organic matter. When soluble sodium nitrate is used as a fertilizer why does not the first heavy rain wash it all away?
11. How do you account for the fact that silicon dioxide occurs in nature in so many different colors (p. 287)?
12. Ice made directly from natural waters is ordinarily white, while that made from distilled water is clear and colorless. Suggest an explanation for this difference.

CHAPTER XXXIII

THE METALS

Metals. The elements so far considered have nearly all been those whose compounds with oxygen and hydrogen are *acids*. They are called the *acid-forming* elements. Those which we shall now study are known collectively as the *metals*. Their hydroxides are *bases*, and on this account the *metals may be defined as those elements whose hydroxides are bases*. When the hydroxide of a metal or any of the simple salts are dissolved in water, the metal forms the positively charged ion.

Properties of the metals. The metals are all solids, except mercury, which is a liquid. Most metals have a high density, are good conductors of heat and electricity, are notably crystalline in structure, and take a bright polish. With the exception of gold and copper they have a silvery luster. Most of them combine readily with oxygen and sulfur, and their surfaces quickly tarnish on exposure to the air.

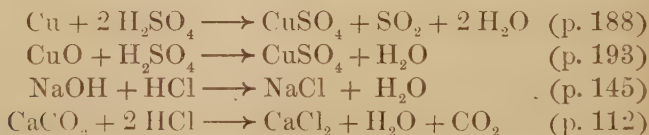
A few of the least active of the metals, such as gold and copper, occur to some extent in nature in the native state. Most of them are found in combination as *oxides*, as *sulfides*, or as salts of various acids, especially as *silicates*. The process of winning metals from their ores is called *metallurgy*. The details of the metallurgy of any given metal must be adapted to the properties of the metal, to the form in which it is found, and to the cost of the operation.

Compounds of the metals. Since the metallic elements are base-forming elements, the compounds which they form are chiefly oxides, hydroxides, and salts of various acids. We

have seen (p. 146) that the number of salts is very large. It will be possible for us to study only the most important of these. With very few exceptions the compounds of the metals are all solids.

Preparation of salts. There are two general ways of preparing salts which are employed so often that it is well to fix them in mind at the outset of the study of metals.

1. **Soluble salts.** If a given salt is *soluble* it can usually be prepared in solution by treating the proper metal, or its oxide, hydroxide, or carbonate, with the proper acid. All these reactions have already been illustrated repeatedly:



2. **Insoluble salts.** A very large number of salts are insoluble in water, and these can be made by *precipitation*. All that it is necessary to do is to bring together in solution two salts, one of which contains the desired metallic ion and the other the negatively charged ion. If, for example, it is known that silver chloride is insoluble in water, it is to be expected that this salt will be precipitated on mixing a solution of any silver salt, such as silver nitrate, with that of any chloride, such as sodium chloride, thus:



Electrochemical industries. To an ever-increasing extent electrical energy is being used both in the separation and the refining of the metals and for the production of many compounds. Such methods have in a number of instances already been mentioned. Naturally these industries tend to develop most extensively in localities where water power is abundant.

Norway has many electrochemical industries. Those of the United States and Canada center at Niagara Falls, the extensive power plants being shown in Fig. 178.

Solubility of salts. It will be seen that a knowledge of the solubility of various salts is of great importance if one wishes to devise a means of preparing a given salt. Fortunately it



FIG. 178. Electrochemical power plants at Niagara Falls

is possible to put into brief form the facts relating to the solubility of the common salts, and these rules will have constant application in the pages which follow.

1. **Hydroxides.** All *hydroxides are insoluble* except those of ammonium, sodium, potassium, calcium, barium, and strontium.

2. **Nitrates.** All *nitrates are soluble*.

3. **Chlorides.** All *chlorides are soluble* except silver and mercurous chlorides. (Lead chloride is soluble in hot water.)

4. **Sulfates.** All *sulfates are soluble* except those of lead, barium, and strontium. (Sulfates of silver and calcium are only moderately soluble.)

5. **Sulfides.** All *sulfides are insoluble* except those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are insoluble in water,

but are changed by water into acid sulfides which are soluble. On this account they cannot be prepared by precipitation.

6. *Carbonates, phosphates, and silicates.* All normal *carbonates, phosphates, and silicates* are *insoluble* except those of ammonium, sodium, and potassium.

EXERCISES

1. Make a list of the elements so far studied. How many are gases under ordinary conditions? How many are liquids?

2. What elements studied are prepared commercially through the agency of electricity?

3. Why cannot sodium be produced by the electrolysis of a solution of its salts? In general, what metals could be so produced?

4. What is the connection between water power and the production of metals and their compounds?

5. Suppose you have on hand hydrochloric acid and marble (p. 112) and wish to prepare some calcium chloride for drying gases (p. 35). How would you proceed?

6. Ordinary copperas has the formula $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. To what class of substances does this compound belong? What materials would you require for its preparation?

7. Suppose you wished to prepare some potassium iodide for medicinal use and had on hand potassium hydroxide. (a) What other compound would you require? (b) Describe the process. (c) Show that the reaction you employ would go to completion (or nearly so).

8. Ferric hydroxide ($\text{Fe}(\text{OH})_3$) is a reddish solid. (a) Is it soluble in water (p. 303)? (b) How could you convert the copperas, prepared according to Ex. 6, into ferric hydroxide?

9. Suppose you mixed solutions of sodium carbonate (Na_2CO_3) and calcium chloride (CaCl_2). (a) Should you expect any reaction to take place? (b) Explain.

10. The hydrate of copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) is commonly known as *blue vitriol*. Suggest a method for making it.

CHAPTER XXXIV

THE SODIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FIRST PREPARED
Lithium . .	Li	6.94	0.534	186°	Arfvedson, 1817
Sodium . .	Na	23.00	0.971	97°	Davy, 1807
Potassium . .	K	39.10	0.862	62°	Davy, 1807
Rubidium . .	Rb	85.45	1.53	38°	Bunsen, 1861
Cæsium . .	Cs	132.81	1.87	26°	Bunsen, 1860

The family. These elements, known as the very light metals, constitute a family in Group I in the periodic table. The name *alkali metals* is often applied to the family for the reason that the hydroxides of the most familiar members of the family (namely, sodium and potassium) have long been called *alkalies*. Sodium and potassium are the only important members of the family. We have already studied sodium (Chapter XVI), and it is advisable for the student to review that chapter in connection with the present one.

COMPOUNDS OF SODIUM

Introduction. Everyone is familiar with some of the metals such as silver, lead, copper, and iron because of their use as metals in our daily lives. In other cases few of us have ever seen the metal, but its compounds are very well known. Sodium is a metal of this kind. As a metal it is a curiosity to most of us, but we all know something about salt, lye, soda, soap, and glass, and these are all compounds of sodium. We have already studied sodium hydroxide as an example of a

typical base (Chapter XVI). We shall now study some other important compounds of sodium. Nearly all these are white crystalline solids.

Sodium chloride (common salt) (NaCl). Sodium chloride, or common salt, is very widely distributed in nature. Thick strata, evidently deposited by the evaporation of salt water, are found in many places. In the United States the most important localities for salt are New York, Michigan, Ohio,



FIG. 179. The evaporation of salt brine in the open air

and Kansas. Sometimes the salt is mined (Fig. 81), especially if it is in the pure form called *rock salt*. More frequently a strong brine is pumped from deep wells sunk into the salt deposit. The brine is evaporated either by heating or, in the preparation of the coarser grades of salt, by simply exposing the brine to the air (Fig. 179). Salt crystallizes in the form of small cubes.

Uses of salt. Since salt is so abundant in nature it is used in the preparation of nearly all compounds containing either sodium or chlorine. These include many substances of the highest importance to civilization, such as soap, glass, hydrochloric acid, soda, and bleaching powder. Enormous quantities of salt are therefore produced each year. Small quantities are essential to the life of man and animals.

Pure salt does not absorb moisture; the fact that ordinary salt becomes moist when exposed to air is not due to a property of the salt but to impurities occurring in it, especially to the presence of the chlorides of calcium and magnesium.

Sodium sulfate (Na_2SO_4). This salt is prepared by the action of sulfuric acid upon sodium chloride, hydrogen chloride being formed at the same time (p. 143):

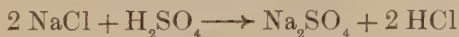


The anhydrous salt is a white solid. It is readily soluble in water, and under ordinary conditions crystallizes as the hydrate $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ (known as *Glauber's salt*). Large quantities of sodium sulfate are used in making sodium carbonate and glass.

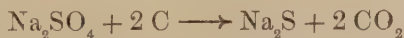
Sodium carbonate (soda ash) (Na_2CO_3). This is the sodium salt of the very weak, unstable carbonic acid (p. 113), but while the acid is unstable, the salt is very stable and is of great importance. There are two different methods now employed in its manufacture, each of which bears the name of its inventor (Figs. 180, 181).

1. **Leblanc process.** This older process, still used in England, involves several distinct reactions, as shown in the following equations:

a. Sodium chloride is first converted into sodium sulfate:



b. The sodium sulfate is next reduced to sulfide by heating it with carbon:



c. The sodium sulfide is then heated with calcium carbonate, when the following reaction takes place:



2. Solvay process. This newer process, and the *only one used in the United States*, consists in passing carbon dioxide and ammonia into a saturated solution of sodium chloride:



The sodium hydrogen carbonate is then filtered off and heated:



The ammonium chloride formed in equation *a* is utilized in once more preparing ammonia.

When sodium carbonate is crystallized from water it forms large crystals of the formula $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, usually known as *washing soda* or *sal soda*. Its solution in water has a mild basic reaction and is used for laundry purposes. Mere mention of the fact that it is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. It is one of the few soluble carbonates.

Historical. In former times sodium carbonate was made by burning seaweeds and extracting the carbonate from their ash. On this account the salt was called *soda ash*, a name still in common use. During the French Revolution this supply was cut off, and in behalf of the French government Leblanc (Fig. 180) made a study of preparing the carbonate directly from salt. As a result he devised the method which bears his name and which was used exclusively for many years. It has been replaced to a large extent by the Solvay process, which was devised by the Belgian chemist Solvay (Fig. 181) in 1863.

By-products. The substances obtained in a given process, aside from the main product, are called the *by-products*. The success of many processes depends upon the value of the by-products formed. Thus hydrochloric acid, a by-product in the Leblanc process, is valuable enough to make the process pay, even though sodium carbonate can be made more cheaply in other ways.

Hydrolysis of salts. In connection with neutralization (p. 154) we learned that when an acid and a base are brought



FIG. 180. NICOLAS LEBLANC (1742-1806)

This cut is from a statue erected in Paris in honor of Leblanc. Previous to his time the supply of sodium carbonate came entirely from the ash of seaweeds. Leblanc devised a method for making it from common salt. This proved to be a much cheaper source of the compound. The Leblanc method was long used in the United States and is still used in England

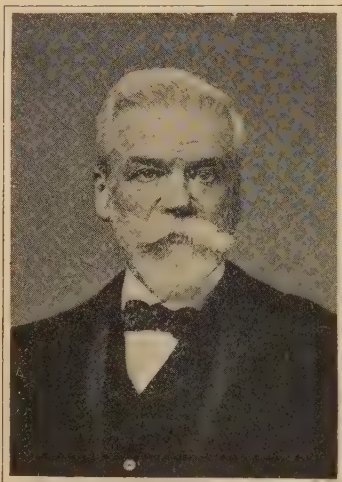


FIG. 181. Ernest Solvay
(1835-1922)

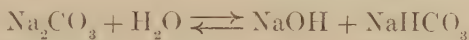
A famous Belgian manufacturing chemist who developed the Solvay process for making sodium carbonate. The commercial success of this process brought Solvay great wealth, and he has been very generous, distributing on his seventy-fifth birthday over a million dollars for educational and philanthropic purposes



FIG. 182. Victor Grignard
(1871-)

A famous French chemist. He discovered a method for making a large number of useful organic compounds, for which discovery he was awarded the Nobel prize in 1912. During the World War the French government sent him to the United States to confer with our chemists on matters pertaining to the war

together in solution the hydroxyl ion of the base and the hydrogen ion of the acid unite to form water, leaving the ions of the salt, which form a neutral solution. From this it might be inferred that solutions of all salts in water are neutral to indicators. This is true if *both acid and base from which the salt is formed are strong ones*. If either is very weak, then the water acts upon the salt and to a slight extent reverses the action of neutralization. Thus in the case of sodium carbonate we have a slight reaction as follows:



The action of water on a salt to form an acid and a base is called hydrolysis. Since the hydrogen of the NaHCO_3 is a part of the *weak acid* H_2CO_3 , it is little ionized, while the NaOH formed is a *strong base* and is very largely ionized. Consequently the resulting solution is *alkaline in reaction*. In general, *all sodium and potassium salts of weak acids are alkaline in reaction*. For a similar reason *all salts of a weak base with a strong acid are acid in reaction*.

Sodium hydrogen carbonate (NaHCO_3). This salt, called *bicarbonate of soda* or *baking soda*, is made by the Solvay process, as explained above, or by passing carbon dioxide into concentrated solutions of sodium carbonate:



It is an essential constituent of all baking powders.

Sodium nitrate (NaNO_3). This substance, known also as *Chile saltpeter*, is found in nature in certain arid regions, where apparently it has been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile (Fig. 183), and most of the nitrate of commerce comes from that country. Smaller deposits occur in California and Nevada. The commercial salt is prepared

by dissolving the crude nitrate (known as *caliche*) in water, allowing the insoluble earthy materials to settle, and evaporating to crystallization the clear solution so obtained. The soluble impurities remain for the most part in the mother liquors.

Since this salt is the only nitrate found extensively in nature, it is the material from which other nitrates, as well as nitric acid, are prepared. Enormous quantities are used as a fertilizer.



FIG. 183. Deposit of sodium nitrate in Chile

Other compounds of sodium. Among the other important compounds of sodium the following may be mentioned: (1) *Sodium thiosulfate* ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$), commonly known as *sodium hyposulfite* or, in photography, simply *hypo*. It is used in photography to dissolve off the plate or film those silver salts that have not been acted upon by the light. (2) *Sodium cyanide* (NaCN) is used in preparing prussic acid (p. 174). Since it readily dissolves gold, it is used in the extraction of gold from its ores. (3) *Disodium phosphate* (Na_2HPO_4) is the most common of soluble phosphates. (4) *Sodium peroxide* (Na_2O_2) is a strong oxidizing agent and evolves oxygen when brought in contact with water. (5) *Sodium iodide* (NaI) and *sodium bromide* (NaBr) are used in medicine and photography. (6) *Sodium sulfite* (Na_2SO_3) is used as a preservative. Thus, when added to ground meat, it not only preserves the meat but causes it to retain the red appearance of fresh meat.

POTASSIUM

Preparation and properties. Potassium is prepared by methods similar to those used in the preparation of sodium. It is more active than sodium; otherwise the properties of the two metals are nearly alike.

Occurrence. Potassium is a rather abundant element, being a constituent of many igneous rocks, such as the feldspars and micas. Very large deposits of the chloride and the sulfate, associated with compounds of calcium and magnesium, are found at Stassfurt, Germany, and are known as the *Stassfurt salts*. Similar deposits occur in Alsace, France.

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. Its soluble compounds are absorbed by growing plants and built up into complex vegetable tissues; when these are burned, the potassium remains in the ash in the form of carbonate. The crude carbonate can be separated from wood ashes by dissolving it in water. This was formerly the chief source of potassium compounds, but they are now prepared mostly from the natural deposits in Germany and France.

The natural deposits consist of definite minerals (Fig. 184), the most important of which are the following:

Sylvite	KCl
Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$
Kainite	$\text{KCl} \cdot \text{MgSO}_4 \cdot 3 \text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$

Compounds. The compounds of potassium are so similar in properties to the corresponding compounds of sodium that for many purposes for which they are used they can be interchanged. The compounds of potassium, being as a rule more expensive, are not so widely used as those of sodium. The methods of preparation are in general the same as those used in preparing the corresponding compounds of sodium.

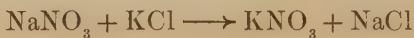
Potassium chlorate (KClO_3). This salt can be made by the action of chlorine on hot solutions of potassium hydroxide. The reaction is somewhat complex, as shown by the following equation:



FIG. 184. The most important of the minerals constituting the Stassfurt salts

It is a white crystalline substance and is used chiefly as an oxidizing agent in the manufacture of matches, fireworks, and explosives; it is also used in the preparation of oxygen and in medicine.

Potassium nitrate (saltpeter) (KNO_3). This salt is found in some regions where the climate is hot and dry, being formed by the decay of nitrogenous organic matter in the presence of earthy material containing compounds of potassium. The salt-peter used in making gunpowder was formerly made by imitating these conditions. At present it is prepared by the action of sodium nitrate upon potassium chloride (the former compound being obtained from Chile and the latter from Germany or France).



This reaction can be made to work because, of the four compounds involved in the reaction, sodium chloride is the least soluble in boiling water and because its solubility is about the same in cold as in hot water (Appendix). Hence, if boiling saturated solutions of sodium nitrate and potassium chloride are mixed, sodium chloride will form and largely precipitate. When the solution is cooled, the potassium nitrate will then crystallize.

Potassium nitrate is a white solid. It is an excellent oxidizing agent and is chiefly used in the manufacture of gunpowder. Smaller amounts are used in medicine and as a preservative for meats.

The question might naturally arise as to the reason for using potassium chlorate and potassium nitrate in place of the corresponding compounds of sodium. The reason is that sodium chlorate is difficult to prepare pure because it is very soluble, while sodium nitrate attracts moisture from the air and therefore is not adapted for the manufacture of gunpowder, which must be kept dry.

Other compounds of potassium. *Potassium hydride* or *caustic potash* (KOH) is a strong base. *Potassium chloride* (KCl), *potassium bromide* (KBr), and *potassium iodide* (KI) are all white solids. The bromide and the iodide are both used in the preparation of photographic reagents and in medicine. *Potassium carbonate* (K_2CO_3), *potassium bicarbonate* (KHCO_3), *potassium sulfate* (K_2SO_4), and *potassium bisulfate* (KHSO_4) are all well-known compounds. They are white solids, readily soluble in water.

Sources of potassium salts in the United States. The great use of potassium salts is for fertilizer. Previous to the World War practically all our supply came from Germany. Indeed, when war was declared Germany counted on starving us, since we could not get these compounds from her. During the period of the war an effort was made to develop adequate supplies of potassium compounds within our borders. In this we were only partially successful, a certain amount being obtained from some of the salt lakes in Nebraska, from minerals, and from other minor sources.

Deliquescent compounds. We have seen that certain compounds such as calcium chloride (p. 35) and sodium nitrate attract moisture and become damp on exposure to moist air. Such compounds are said to be *deliquescent*.

THE AMMONIUM COMPOUNDS

Composition. As explained in a previous chapter, when ammonia is passed into water the two combine to form the base NH_4OH , known as *ammonium hydroxide*. When this base is neutralized with acids, there are formed the corresponding salts, known as the *ammonium salts*. Since the ammonium radical is univalent, ammonium salts resemble those of the alkali metals in their formulas; they also resemble the latter salts very much in many chemical properties and may be conveniently described in connection with them. Among the ammonium salts the chloride, sulfate, carbonate, and sulfide are the most familiar.

Ammonium chloride (sal ammoniac) (NH_4Cl). This is a white solid. When heated it partly decomposes into ammonia and hydrogen chloride, which recombine as the temperature falls:

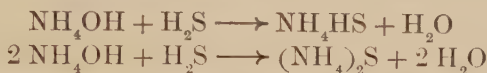


This salt is used in soldering, since the hydrogen chloride evolved by the heat removes the oxide from the surface of the metals. It is also used in making dry cells, in medicine, and as a chemical reagent.

Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). This salt is prepared at low cost by passing ammonia into sulfuric acid. It is especially valuable as a fertilizer, and large quantities are used for this purpose.

Carbonates of ammonium. Both the normal carbonate $(\text{NH}_4)_2\text{CO}_3$ and the acid carbonate NH_4HCO_3 are white solids, readily soluble in water. They are important chemical reagents.

Ammonium sulfides. When hydrogen sulfide is passed into aqua ammonia a solution containing ammonium sulfide $((\text{NH}_4)_2\text{S})$ and ammonium acid sulfide (NH_4HS) is obtained:



This solution is usually known simply as ammonium sulfide and is used in chemical analysis as a reagent in testing for certain metals.

Flame reactions. A number of the metals when volatilized in a colorless flame, such as that of a Bunsen burner, impart a characteristic color to the flame. Thus sodium (or any of its compounds that will volatilize in the heat of the flame) makes the flame yellow. Potassium and its compounds color the flame a pale violet, and lithium colors it a deep crimson red.

Advantage is taken of these facts in testing for the presence of the elements in different substances. The test is best made by using a platinum wire, one end of which is fused into a piece of glass tubing that serves as a handle. The other end of the wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance), and the wire with the adhering particles is held in the outer edge of the base of the Bunsen flame (Fig. 185). The light from the sodium flame is absorbed in passing through blue glass, while that from potassium is not absorbed. Advantage is taken of this difference in detecting the two elements in mixtures.

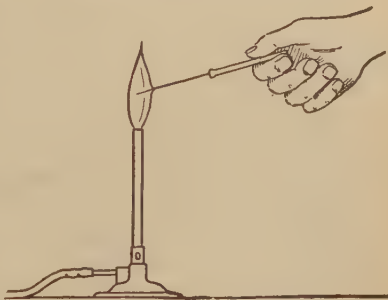


FIG. 185. Making a flame test

EXERCISES

1. What is an alkali? Can a metal itself be an alkali?
2. Do the alkali metals show any gradation of properties corresponding with their atomic weights? (Consult table at head of chapter.)
3. (a) Which of the alkali metals will float on water? (b) Which will melt in boiling water?
4. How should you expect potassium to act on water?
5. What substances should you expect to result from the electrolysis of a solution of potassium chloride?
6. What nonmetallic element is obtained commercially from the deposits of Chile saltpeter?
7. How can you change sodium carbonate into sodium bicarbonate and vice versa?
8. The sodium chloride used for table salt is often mixed with a little flour or starch. Explain the reason for this.
9. Ammonium chloride is a by-product of the Solvay process. How could you prepare from this the ammonia used in the process (p. 161)?
10. Carbonic acid (H_2CO_3) (p. 113) is a very weak and very unstable acid. How do you account for the fact that a solution of sodium carbonate is basic?
11. (a) Why are the carbonates such as sodium carbonate and calcium carbonate so easily acted upon by acids? (b) How could you test for the presence of a carbonate?
12. Write the equation for the reaction between sodium carbonate and hydrochloric acid.
13. Why is sodium hydrogen carbonate used in fire extinguishers (p. 113)?
14. The solution obtained by treating wood ashes with water is strongly basic. Explain.
15. (a) What part did Chile saltpeter play in the World War? (b) How did Germany get along without it?
16. (a) Suppose you passed chlorine into a hot solution of potassium hydroxide, what products are formed (p. 312)? (b) If you were to heat the products, what single compound would be left?
17. Bromine and iodine act upon potassium hydroxide (and sodium hydroxide) just as chlorine does. How could you prepare (a) potassium bromide? (b) sodium iodide?

18. State what substances already studied are prepared from the following compounds: (a) ammonium chloride; (b) ammonium nitrate; (c) sodium nitrate; (d) potassium chlorate.

19. 100 kg. of Glauber's salt contains what weight of water of crystallization?

20. 100 lb. of sodium carbonate is dissolved in water and crystallized. (a) What is the common name of the resulting product? (b) Calculate the weight of the product.

21. If you used large quantities of sal soda and had to have it shipped a long distance, what economy would suggest itself to you?

22. Borax (p. 291) has a mild alkaline reaction. Can you explain this?

23. What weight of sodium carbonate can be prepared from 1 ton of sodium chloride (a) by the Leblanc process (note that 2 gram-molecular weights of sodium chloride give 1 gram-molecular weight of sodium carbonate; see equation, p. 307)? (b) by the Solvay process?

24. Supposing that the fire extinguisher shown in Fig. 68 (p. 113) contained 5 kg. of sodium bicarbonate in solution, what volume of carbon dioxide would be evolved in using the extinguisher? Equation:



25. Suppose you wished to operate a plant built for the manufacture of 3 tons of saltpeter daily. (a) What compounds should you require for its manufacture? (b) Calculate the daily consumption of each of these compounds in your factory, assuming that you could obtain 100 per cent yields.

26. Suppose you were given 1000 g. of sal soda and told to convert it into caustic soda, (a) how would you proceed (p. 153)? (b) what other materials would you require? (c) what weight of sodium hydroxide would you expect to obtain?

CHAPTER XXXV

SOAP; GLYCERIN; EXPLOSIVES

Introductory. At first thought one might wonder why three products so different from each other as are soap, glycerin, and explosives should be brought together for study in one chapter. However, the grouping is a natural one industrially, for glycerin is a by-product in the manufacture of soap; and nitroglycerin, one of the most powerful explosives, is prepared from glycerin and stands in a general way as a type of an explosive compound.

Composition of soap, and materials used in its preparation. Ordinary soap is a mixture of the sodium salts of oleic, palmitic, and stearic acids (pp. 259, 262). The essential materials used in the preparation of soap are as follows:

1. **Fat or oil.** As shown on page 262, *fats and oils are largely mixtures of olein, palmitin, and stearin*. The cheaper grades of these are used in making soap. Those commonly employed are a low grade of animal fat (tallow) and the cheaper vegetable oils, such as cottonseed oil, coconut oil, and palm oil (Fig. 186). Some resin (p. 408) is used in the cheaper grades of soap as a substitute for the fat.

2. **Alkali.** The alkali used is the hydroxide of either sodium or potassium. Sodium hydroxide is nearly always used, since it gives a hard soap, while potassium hydroxide gives a soft soap.

Reaction taking place in the preparation of soap. When the fat and alkali are heated together under proper conditions, the olein, palmitin, and stearin present in the fat are decomposed, forming glycerin, together with sodium oleate, sodium

palmitate, and sodium stearate. *A mixture of these three salts constitutes soap.* The reactions may be illustrated by the following equation, which represents the change taking place when stearin is heated with sodium hydroxide:



In this reaction the fat (stearin, palmitin, olein) is said to be *saponified*, and the process is known as *saponification*.

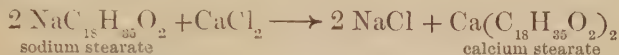


FIG. 186. Some common substances used in the manufacture of soap

Commercial manufacture of soap. The oil or melted fat is poured into large iron kettles together with a solution of sodium hydroxide containing about one fourth of the amount of alkali necessary to saponify the fat. As a rule the kettles are very large (Fig. 187), 500,000 lb. or more of soap being made in some of them in a single heating. They are provided with coils of steam pipe for heating the mixture. The fat and alkali are stirred by forcing air or live steam into the bottom of the mixture. As the heating continues the remainder of the alkali is added. The reaction is complete in from two to five days.

The soap is next removed, or *salted out* (p. 296), from the mixture. This process consists in adding salt and again heating. After a time the soap rises to the top of the liquid (or *spent lye*, as it is called). The soap so obtained is purified and then run into

a calcium or magnesium compound is added to a colloidal solution of soap (Fig. 188):

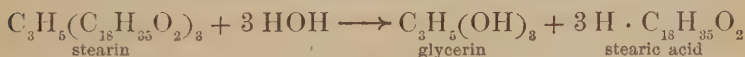


It is due to this fact that soaps do not lather with hard waters but form a curdy precipitate, since such waters always contain calcium and magnesium salts in solution.

The cleansing action of soap is not thoroughly understood, but seems to be associated with the property which soap possesses of forming emulsions (p. 297). When soap is rubbed on the skin any oily substances present are emulsified and washed away.

Candles. When fats are heated with

steam they are decomposed into glycerin and free acid as follows:

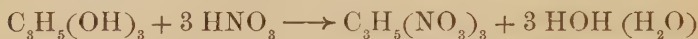


The solid fatty acids thus obtained, mixed with paraffin, are used in making candles. The glycerin set free in this process, as well as that set free in the process of soap-making, is easily recovered, and it is in this way that our commercial supplies of glycerin are obtained.



FIG. 188. When solutions of soap and a calcium salt are mixed, a white precipitate of calcium stearate forms

Glycerin ($C_3H_5(OH)_3$). This is a colorless oily liquid having a sweet taste. Nitric acid reacts with it just as with a base, forming the nitrate $C_3H_5(NO_3)_3$:



The nitric acid used in this reaction is mixed with a little sulfuric acid, the latter serving to absorb the water produced. The resulting nitrate is a slightly yellowish oil commonly known as *nitroglycerin*. It is very explosive and is used in the manufacture of dynamite.

Utilization of garbage. Many cities now treat their garbage in such a way that it becomes a source of revenue rather than expense. The garbage is first heated with steam and hot water. This causes the oils and fats to collect as a liquid on the top of the hot water so that they can easily be removed. The residue makes a valuable fertilizer, while the fats and oils are used in making candles, soap, and glycerin.

Explosives. An explosion is caused by a very rapid chemical reaction which results in the formation of a large volume of gas from a comparatively small volume of liquid and solid materials called *explosives*. The greater the volume change and the more rapidly it is produced, the more violent the explosion.

For a brief discussion we may divide explosives into two groups: namely, (1) gunpowder and (2) nitro-explosives.

1. **Gunpowder.** Ordinary gunpowder is an intimate mixture of potassium nitrate, sulfur, and charcoal. When they are ignited, complicated reactions occur and a number of products are formed, about half of which are solid and the remaining half gases. The chief of these products are carbon dioxide, nitrogen, and the carbonate, sulfate, and sulfide of potassium.

2. **Nitro-explosives.** These are compounds of carbon, hydrogen, oxygen, and nitrogen. When they are exploded, the carbon and hydrogen unite with the oxygen to form oxides of carbon and water vapor, while the nitrogen is liberated in the free state. These explosives are all made by the action of a mixture of

nitric and sulfuric acid upon certain compounds, the name of the explosive ordinarily indicating the compound used. The most important of the nitro-explosives are given below:

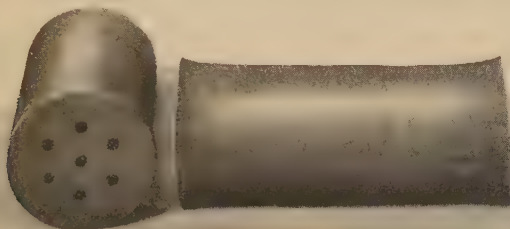


FIG. 189. Powder grains for large guns (natural size)

(a) *Nitrocellulose*. Approximate composition, $C_6H_7O_2(NO_3)_2$. This substance (p. 246) is a far more powerful explosive than gunpowder. If ignited, it will, under ordinary conditions, burn quietly. If subjected to a sudden shock (such as may be produced by the explosion of a small percussion primer), the nitrocellulose decomposes with enormous violence. The products of the decomposition are all colorless gases; hence the use of this explosive in making *smokeless* gunpowder. When used for this purpose it is necessary to modify the pure material somewhat, as otherwise the violence of the explosion would shatter any firearms in which the powder was used. This is done by mixing nitrocellulose with sufficient alcohol and ether to form a jelly. This is then molded into the form of rods (grains), with a number of perforations through the rods. The size of the grains varies with the size of the guns in which the powder is used. Fig. 189 shows the form of the grains used in the large guns of our navy.



FIG. 190. A stick of dynamite with fuse attached

(b) *Nitroglycerin* ($C_3H_5(NO_3)_3$). This compound (p. 322) resembles nitrocellulose in the violence of its explosive effects. The changes taking place in its decomposition are represented in a general way by the following equation:



One volume of nitroglycerin yields on explosion about 1300 volumes of gas, which is expanded by the heat of the reaction to over 10,000 volumes. Pure nitroglycerin is very dangerous because

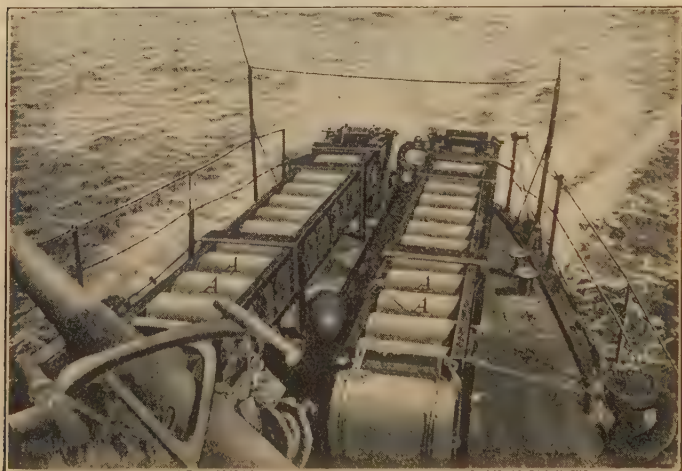


FIG. 191. Rows of depth bombs (A, A, A, A) on the rear of a submarine destroyer

It was these destroyers and bombs which overcame the submarine menace in the World War

of the ease with which it is set off. Large quantities are used in making *dynamite*, in which form it is not exploded so readily by jarring and can be transported with less danger. Ordinary dynamite (Fig. 190) consists of a mixture of sodium nitrate, nitroglycerin, and wood pulp, the latter acting like a sponge to absorb the nitroglycerin. *Gelatin dynamite* consists of nitrocellulose and nitroglycerin mixed together to form a jelly. It is a very powerful explosive, since it contains no inert material.

(c) *Trinitrotoluene* ($C_7H_5(NO_2)_3$). This explosive, commonly known as T.N.T., is a white solid, but colors on exposure to air. It is too powerful to be used in guns, but is especially adapted for use in bombs and torpedoes. It was largely used in the World War. Fig. 191 shows two rows of depth bombs (*A, A*) on the rear of a submarine destroyer. Each bomb contains about 300 pounds of T.N.T. If a submarine was known to be in a certain locality, these bombs were dropped into the water at that point, from the stern of the rapidly moving destroyer, and the pressure of the water caused them to explode when they reached a certain depth.

(d) *Picric acid* or *trinitrophenol* ($C_6H_2OH(NO_2)_3$). This is a yellow solid (p. 234) and was the favorite explosive of the French in the World War. Large quantities were made in the United States and shipped to France.

EXERCISES

1. Illustrate the meaning of the term *by-product*, using the soap industry as an example.

2. Could calcium hydroxide be used as the alkali in soap manufacture?

3. Write the equation for the reaction (*a*) between olein and sodium hydroxide: (*b*) between palmitin and potassium hydroxide.

4. (*a*) To what class of substances (acid, base, or salt) does soap belong? (*b*) Account for the fact that a solution of soap reacts basic (p. 308).

5. Can you suggest any reason for the cleansing properties (*a*) of aqua ammonia? (*b*) of borax? (*c*) of sodium carbonate?

6. Should you expect soap to lather in rain (cistern) water?

7. Do you see any reason for adding naphtha to soap as is done in making naphtha soaps?

8. Families used to make their soap by heating the fat refuse of foods with a solution prepared by extracting wood ashes with water.

(*a*) What was the alkali used (p. 311)? (*b*) What kind of soap resulted?

9. What effect does the softening of a city water supply have upon soap consumption?

10. Give the steps in making candles from garbage.

11. Sodium nitrate is much less expensive than potassium nitrate. Why not use it in making gunpowder?

12. Why are the nitro-explosives more powerful than gunpowder?

13. Why are some powders smokeless and others not?

14. (a) Has T.N.T. sufficient oxygen to burn completely the carbon and hydrogen present? (b) Account for the fact that when T.N.T. explodes, great volumes of black smoke are formed.

15. Should you expect the following explosives to be smokeless: (a) nitroglycerin? (b) picric acid?

16. (a) Why did not the Germans use nitroglycerin explosives during the World War? (b) Where did they obtain the nitric acid necessary for making explosives?

17. Calculate the percentage of nitrogen (a) in nitroglycerin; (b) in T.N.T.

CHAPTER XXXVI

THE CALCIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	FORMULA OF CHLORIDE
Calcium	Ca	40.07	1.55	CaCl_2
Strontium	Sr	87.63	2.54	SrCl_2
Barium	Ba	137.37	3.75	BaCl_2

The family. The calcium family consists of the very abundant metal calcium and the rarer metals, strontium and barium. Like the alkali metals, they are acted upon by both water and air, and on this account do not occur in a free state in nature. They are bivalent, so that the formulas of their salts differ from the formulas of the corresponding salts of the alkali metals.

CALCIUM

Introduction. The metal calcium, like sodium and potassium, is little used, but its compounds are numerous and abundant. Its most familiar compounds are calcium carbonate in the form of *limestone* and *marble*, and calcium phosphate, which occurs abundantly in nature and constitutes the mineral constituents of our bones. The metal itself is silver-white and light in weight but quite hard. It is prepared by the electrolysis of its melted chloride. It burns in oxygen with dazzling brilliancy and, like sodium, decomposes water, forming calcium hydroxide and hydrogen.

Calcium carbonate (CaCO_3). Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form and sometimes constitutes whole mountain ranges.

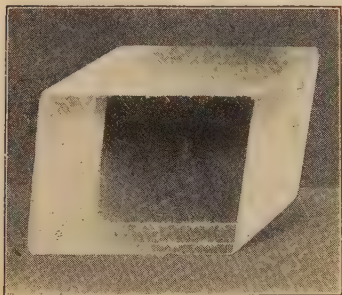


FIG. 192. A crystal of Iceland spar

Limestone is never pure calcium carbonate, but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. *Pearls, coral,* and various *shells* are largely calcium carbonate. *Calcite* is a very pure, crystalline form and often is found in large transparent crystals (Fig. 192) called *Iceland spar*. *Marble* is composed of very small calcite crystals.

In the laboratory pure calcium carbonate can be prepared by mixing solutions of a calcium salt and some carbonate:



When prepared in this way it is a soft white powder often called *precipitated chalk*, and is much used as a polishing powder (tooth powder).

The natural varieties of calcium carbonate find many uses, as in the preparation of lime and of carbon dioxide; in metallurgical operations, especially in making iron and steel; in the manufacture of soda and glass; for building-stone and as ballast for roads.

Calcium acid carbonate ($\text{Ca}(\text{HCO}_3)_2$). Calcium carbonate is almost insoluble in pure water. It readily dissolves, however, in water which holds carbon dioxide in solution (p. 113). This is due to the fact that the carbonate combines with the carbonic acid present in the water to form calcium acid carbonate, which is soluble:



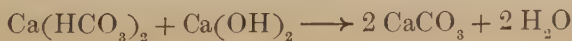
The resulting acid carbonate exists only in solution, since it is unstable and decomposes into the normal carbonate on heating or on evaporation of its solution.

Formation of caves. Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, being held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation in limestone rock of large caves, such as the Mammoth Cave in Kentucky. Water trickling through the roofs of these caves evaporates, leaving a deposit of calcium carbonate, which, as the process continues, often forms icicle-shaped masses known as *stalactites*; or the water may drip upon the floor of the cave, forming similar masses known as *stalagmites* (Fig. 193).



FIG. 193. Stalactites and stalagmites

Commercial methods for softening water. Ordinary hard waters, such as well and river waters, contain not only the acid carbonates of magnesium and calcium but also the chlorides and sulfates of these metals, together with small quantities of other salts. Experiments have shown that such waters may be softened by the addition of calcium hydroxide and sodium carbonate (Fig. 194). The calcium hydroxide converts the acid carbonates of calcium and magnesium into the normal carbonates, which, being insoluble, settle out:



The sodium carbonate used converts the chlorides and sulfates of calcium and magnesium into the insoluble carbonates:



Water softened in this way contains sodium sulfate and chloride, but these salts are not objectionable.

*Tank containing solution
of $\text{Ca}(\text{OH})_2$ and Na_2CO_3*

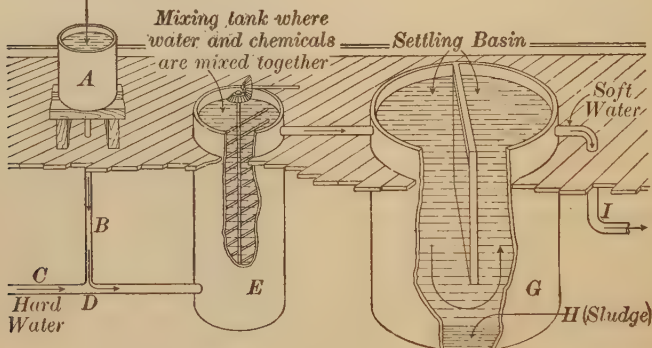
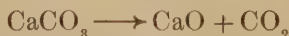


FIG. 194. Softening water on a large scale

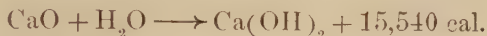
The compounds used flow from the container *A* through the pipe *B*, and at *D* meet the hard water entering through *C*. The compounds and water flow into the tank *E*, where they are mixed by stirring and interact with each other. The water and the insoluble products formed then flow into the settling basin *G*. Here the insoluble products settle to the bottom (*H*) and are drawn off from time to time, while the soft water escapes through the pipe *I*.

Calcium oxide (lime) (CaO). Pure calcium oxide can be prepared by burning calcium or by heating its carbonate. The more or less impure oxide (commercially known as *lime* or *quicklime*) is always prepared by strongly heating limestone in large furnaces called *limekilns*:



Lime, when pure, is a white amorphous substance. It melts only in the heat of the electric furnace. Water acts upon lime with the evolution of a great deal of heat, — whence

the name *quicklime*, or *live lime*, — the process being called *slaking*. The equation is



Because of its affinity for water it is used to dry gases. It also absorbs carbon dioxide, forming the carbonate. Lime exposed to air is therefore gradually converted into the hydroxide and then into the carbonate, and will no longer slake with water. It is then said to be *air-slaked*. Lime is produced in enormous quantities for use in making calcium hydroxide.

Commercial production of lime. A vertical section of the newer form of limekiln is shown in Fig. 195. The kiln is about 50 ft. in height. A number of fire boxes, or furnaces *A, A*, are built around the lower part, all leading into the central stack. The kiln is filled with limestone through a swinging door *B*. The hot products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*, and this serves the double purpose of cooling the hot lime at the base of the furnace and of furnishing heated oxygen for the combustion. The lime is dropped into cars run under the furnace. Ordinarily a number of these kilns are operated together, as shown in Fig. 196.

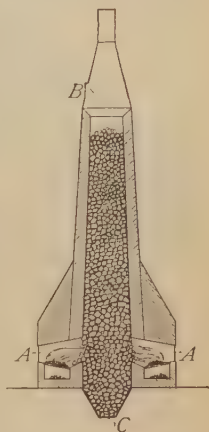


FIG. 195. A vertical section of a modern limekiln

Calcium hydroxide (slaked lime, hydrated lime) (Ca(OH)_2). This compound is prepared by adding water to lime, as explained above. When pure it is a light white powder. It is sparingly soluble in water, forming a solution called *lime-water*. Owing to its cheapness it is used in the industries whenever an alkali is desired. It is used in the preparation of ammonia, bleaching powder, and the hydroxides of

sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from coal gas, to remove the hair from hides in making leather, for making mortar and plaster, and for neutralizing the acids in soils (p. 335).



FIG. 196. A group of limekilns in a modern plant

Mortar and plaster.

Mortar is a mixture of calcium hydroxide and sand. When it is exposed to the air or spread upon porous materials, moisture is removed from it (partly by absorption into the porous materials and partly by evaporation) and the mortar becomes firm,

or *sets*. At the same time carbon dioxide is slowly absorbed from the air and hard calcium carbonate is formed :



By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous. It also prevents too much shrinkage. Plaster is a mixture of calcium hydroxide and hair or wood fiber, the latter serving to hold the mass together.

Bleaching powder. When chlorine is passed over calcium hydroxide there is formed a white solid compound having the formula CaOCl_2 and known as *bleaching powder*, *chloride of lime*, or simply *bleach*:



When this compound is treated with an acid, chlorine is evolved:

$$\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2$$

When exposed to the air bleaching powder is slowly acted upon by moisture and carbon dioxide, evolving hypochlorous acid, which is a good disinfectant. Bleaching powder is prepared in large quantities for use as a bleaching agent, as a disinfectant, and as an agent for purifying city water-supplies.

In the commercial preparation of bleaching powder the calcium hydroxide is spread to a depth of 2 or 3 inches upon the floor of a room, usually made of lead or concrete (Fig. 197). The chlorine enters near the top at *A*. Any unabsorbed chlorine passes out at

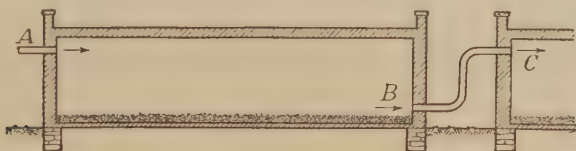


FIG. 197. Chambers for the manufacture of bleaching powder

B and into the adjoining chamber at *C*. The commercial product ordinarily contains about 35 per cent of chlorine. It is shipped in sealed packages or iron drums.

Calcium sulfate (CaSO_4). Calcium sulfate occurs in nature in several different forms, the most common of which is *gypsum* ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This is quarried in large amounts in New York, Iowa, and Michigan. It is used as a filler in making paper (p. 250), as a constituent of fertilizers, and especially in making *plaster of Paris*. It is but slightly soluble in water.

Plaster of Paris ($(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$). This is a fine white powder obtained by carefully heating gypsum. When water is added to the powder a plastic mass is formed which quickly hardens, or *sets*. This property makes it valuable for molding casts, for stucco work, and for a finishing coat on plastered walls. Broken bones are often held in place by casts of plaster of Paris until they grow together.

Calcium carbide (CaC_2). This compound is prepared on a large scale for use in the manufacture of acetylene (p. 215) and in making fertilizers. It is made by heating a mixture of lime and coke in an electric furnace:



The pure carbide is a colorless, transparent solid. The commercial article is a dull-gray porous substance which contains many impurities. It is placed on the market in air-tight containers.

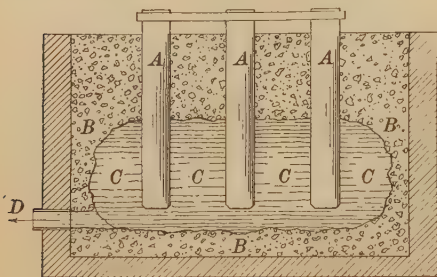


FIG. 198. A furnace for making calcium carbide

The general principles involved in its preparation are illustrated in Fig. 198. A large brick room open at the top is fitted with carbon electrodes *A, A, A* and filled with a mixture, *B*, of lime and coke. Sufficient current is used to secure a temperature of about 2000° . The carbide melts as fast as it forms, *C, C*, and is drawn off from time to time at *D*.

Calcium cyanamide (CaCN_2). When nitrogen is passed over hot calcium carbide the two react, forming a compound known as *calcium cyanamide*:



The commercial product is impure, containing about 60 per cent of the calcium cyanamide; the impurities are lime and carbon. This is ground, mixed with water (which slakes the lime present), and in this form sold as a fertilizer under the name of *cyanamide*. Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

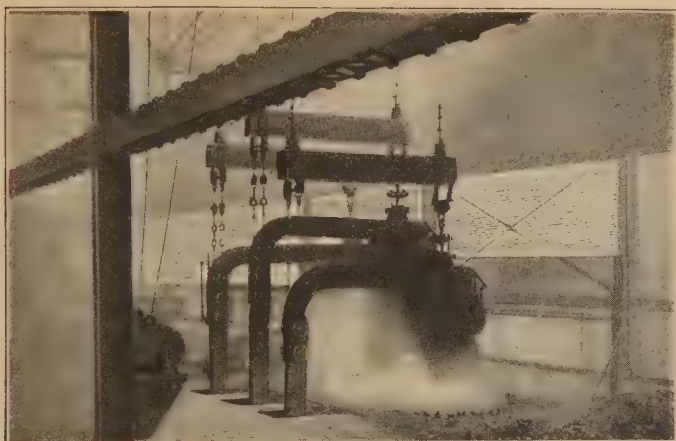


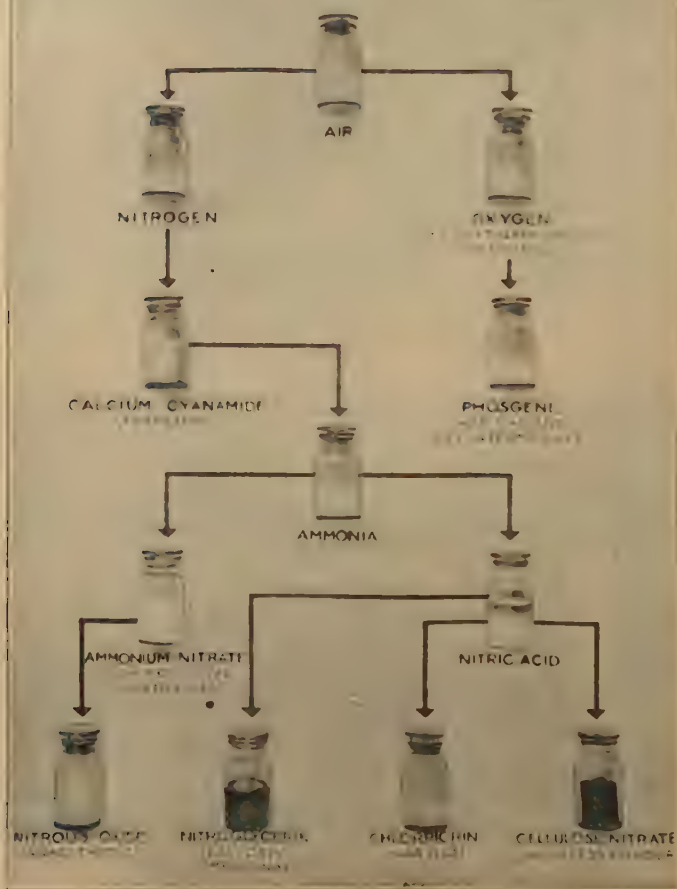
FIG. 199. View in a plant for making calcium carbide, showing the large carbon electrodes which dip into the furnace below



FIG. 200. View in a plant for making calcium cyanamide

Calcium carbide is placed in the perforated steel cans shown in the background. These are then lowered into the furnaces shown in the foreground. The carbide is heated to about 1000° , and then pure nitrogen obtained from liquid air is passed over it, the two combining to form the cyanamide

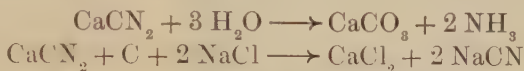
AIR PRODUCTS



CONTINUATION OF SEPARATE SECTION

FIG. 201. Some products obtained from the air during the World War

Calcium cyanamide is also used as a source of ammonia as well as sodium cyanide, thus:



During the World War the government constructed a large plant (costing nearly \$100,000,000) at Muscle Shoals, Alabama, for preparing ammonia by this process. A part of the ammonia was oxidized to nitric acid (p. 169), and this was then combined with the unchanged ammonia to form ammonium nitrate, which was valuable as an explosive. The plant had a capacity of 300 tons of the nitrate daily. The chart on the opposite page shows some of the products formed from the atmosphere during the war.

Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). This important substance occurs in nature as the mineral *phosphorite* and as a constituent of *apatite*. Large amounts of it occur in the form of *rock phosphate*, which is found especially in Florida, Tennessee, and some of the Western states. It is also the chief mineral constituent of bones. Bone ash is, therefore, nearly pure calcium phosphate.

Other compounds of calcium. *Calcium chloride* (CaCl_2) occurs in sea water and is formed in large quantities as a by-product in the Solvay process for making sodium carbonate. The anhydrous salt readily absorbs moisture and is used as an agent for drying gases. A solution of the salt is used as a brine in the manufacture of ice (p. 166). It has also been used to lay the dust on roads, and mines have been sprinkled with it in the hope of preventing dust explosions. *Calcium acid sulfite* ($\text{Ca}(\text{HSO}_3)_2$) is used in large quantities in the manufacture of paper (p. 250). A number of *calcium silicates* are known, and derive their chief interest from the fact that they are important constituents of cement and glass.

STRONTIUM AND BARIUM

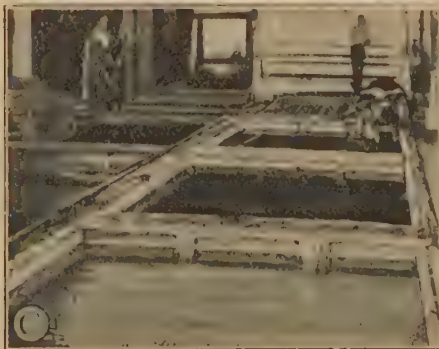
General. These elements are much rarer than calcium, are difficult to prepare, and have no commercial uses. Their compounds resemble those of calcium in composition and properties. Strontium compounds, especially the nitrate, when ignited with oxidizable substances, give a brilliant crimson color and on this account



The hides of animals from which leather is made are treated with salt and stored away in large cellars until they are needed for tanning, as shown in A



The hides are converted into leather by the action of tannin (a complex substance present in the bark of certain trees, especially the oak) or some substance which acts in a similar way. In B are shown the supplies of oak bark stored in the yard of a tannery



Before treatment with tannin, the hides are first soaked in a strong solution of calcium hydroxide (C) to loosen the hair, which is then easily removed

FIG. 202, A, B, and C. The tanning of leather

After the hair is removed the hides are scraped to remove all adhering flesh, as shown in D



As shown in E, the hides are then placed in tanning vats for a number of weeks. These contain water and ground tanbark, the tannin of which slowly changes the hides into the tough, raw or unfinished leather



In F the raw leather is being washed, scoured, ironed, greased, and dyed (if a colored leather is desired). The particular treatment of the raw leather depends upon the kind of leather desired



FIG. 202, D, E, and F. The tanning of leather

are used in the manufacture of red lights. Under similar conditions barium nitrate gives a green light. The following compounds of barium are of importance:

Barium chloride ($\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$). Barium chloride is a white solid. It is used in the laboratory as a reagent to detect the presence of sulfuric acid or soluble sulfates, reacting with these to form the insoluble barium sulfate.

Barium sulfate (barite) (BaSO_4). Barium sulfate occurs in nature as a heavy white mineral known as *barite* or *heavy spar*. It is precipitated as a crystalline powder when a barium salt is added to a solution of a sulfate or to sulfuric acid:

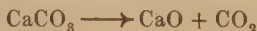


It is used in large quantities in the manufacture of paints.

The tanning of leather. The use of calcium hydroxide in the tanning of leather suggests the brief description of the process given in connection with Fig. 202, *A*, *B*, *C*, *D*, *E*, and *F*.

EXERCISES

1. (a) What properties do the members of the calcium family have in common with the alkali metals? (b) In what respects do they differ?
2. Do the members of the calcium family show any gradation of properties corresponding to their atomic weights? (See table at head of chapter.)
3. What simple test will enable you to tell whether a rock contains a carbonate?
4. Some samples of Iceland spar and gypsum look very much alike. How could you distinguish between them?
5. Beads made of celluloid (p. 246) are often dyed and sold as coral beads. Can you suggest any simple way of detecting the fraud?
6. If you blow exhaled air through limewater, the clear solution becomes cloudy, but as you continue, it clears again. If now you boil the clear solution it again becomes cloudy. Explain.
7. Account for the deposits in teakettles in which hard waters are boiled.
8. (a) Is the reaction represented by the equation



reversible? (b) If so, how can you make it go in either direction?

9. (a) Would lime after long exposure to the air serve for making mortar? (b) Explain.

10. Write the equation for the reaction that takes place when calcium hydroxide is used for liberating the ammonia from ammonium chloride.

11. Enormous quantities of calcium chloride are formed as a by-product in the Solvay process for the manufacture of sodium carbonate (p. 308). Account for its formation.

12. (a) Show how the nitrogen of the atmosphere can be utilized in preparing ammonia through the agency of calcium carbide. (b) In what other way can the same result be obtained (p. 165)?

13. Mention the advantages gained by a city from softening its water supply.

14. Why do calcium and magnesium salts make a water hard, while sodium salts do not?

15. What term do we apply to compounds like calcium chloride that become moist on exposure to air (p. 314)?

16. If you used large quantities of bleaching powder, would you be willing to base the price solely on the weight of the product furnished?

17. In making calcium cyanamide very high temperatures and very low temperatures are utilized. In what connection is each of these temperatures employed?

18. What weight of limestone is burned in a plant which has an output of 25 tons of lime daily?

19. (a) What weight of water is required for slaking 1 kg. of lime? (b) How many calories of heat will be evolved in the slaking?

20. The water used by a certain city contains 120 g. of calcium acid carbonate in 100 gal. of water. (a) What weight of calcium hydroxide is necessary to soften each 100 gal. of the water (see equation, p. 329)? (b) Would it make any difference if you added more than this weight of the calcium hydroxide?

21. A certain factory produces 50 tons of bleaching powder daily. How many pounds of calcium hydroxide are required daily?

22. (a) If bleaching powder is pure CaOCl_2 , what per cent of chlorine would it contain? (b) Compare your result with the amount in the commercial product (p. 333).

23. What weight of gypsum is required in making 1000 kg. of plaster of Paris?

CHAPTER XXXVII

SOILS AND FERTILIZERS

Formation of soils. Soil results from disintegration of rock. Many agencies contribute to this change, prominent among them being the action of water and air. The glaciers



FIG. 203. The formation of soil through the disintegration of rocks

which once covered a large portion of the globe exerted a very powerful grinding effect, breaking off large boulders and reducing them to a powder. Water acts in a number of ways. It finds its way into the cracks and crevices, and on freezing expands and so tends to break the rocks; it dissolves out certain rock constituents so that the remainder of the rock tends to crumble; and running water carrying particles in suspension grinds the rocks

with which it comes in contact. Air also acts upon some rocks chemically, while strong winds carrying sand dust exert a powerful sand-blast effect. When plants get a foothold

they assist greatly, not only by the mechanical action of their roots but also through the chemical action of the various products formed in their decay. The soil is the result of all these agencies acting through long periods of time (Fig. 203).

Different kinds of soil. Since the rocks vary widely in composition, it follows that the resulting soils will vary in a corresponding way. Thus we have limestone soil, formed chiefly

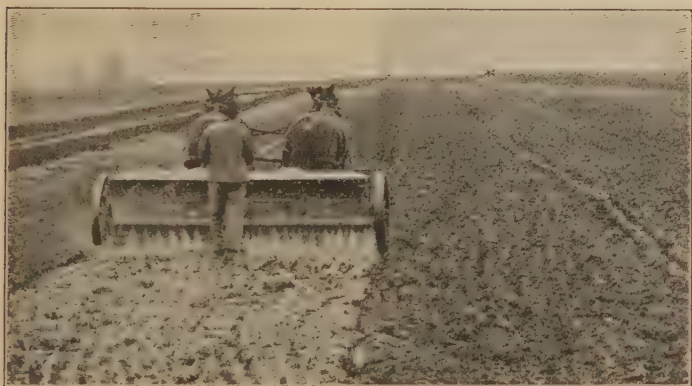


FIG. 204. Neutralizing acidity in soil by an application of calcium hydroxide or ground limestone

by the weathering of limestone; and sandy and clay soils, which are richer in silicates. When plants decay certain acid products are formed, so that soils tend to become acid. Most crops do not thrive on such soil. If the soil contains limestone, the acids will be neutralized as fast as formed and the soil thus kept *sweet*; if the soil does not contain limestone, then ground limestone or calcium hydroxide is added to the soil (Fig. 204).

Soils differ not only in composition but also in their physical properties. Thus, some soils are light and easily allow water and air to circulate through them (these conditions are essential to a fertile soil), while others are compact and

impervious to water. Crops do not thrive on wet soils; hence the necessity of drainage (Fig. 205). A good soil must have many properties of a colloid jelly, in which adsorption of salts and gases plays an important part in holding plant food.

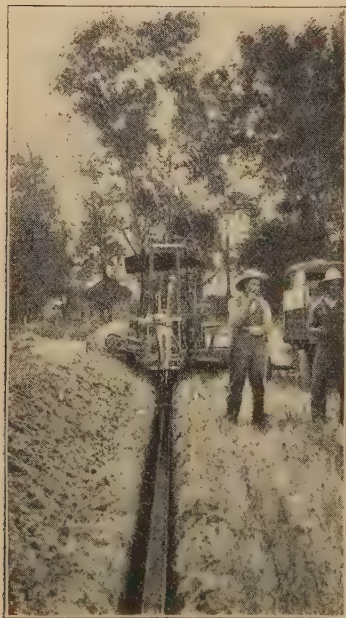


FIG. 205. Draining wet soils so as to make them fertile

Plant food and fertilizers.

With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant derives its nourishment from the soil. In order that vegetation may thrive it is essential, therefore, that the soil should contain an adequate supply of appropriate plant food, and this includes both mineral matter and organic matter (*humus*). Moreover, since this supply is continually being drawn upon by the growing plant, it is necessary, in order that the soil may retain its fertility, that the ingredients so withdrawn shall be returned to it. It is for this purpose that fertilizers are used.

Constituents of fertilizers. While a number of elements are essential to the growth of the plant, experience has shown that in general the fertility of a soil that has the necessary physical properties may be maintained by adding three substances: (1) nitrogenous matter, (2) phosphates of calcium, and (3) compounds of potassium. It seems probable that the element sulfur also plays an important part in the growth of plants, although its action is not thoroughly understood.

Sources of fertilizers. The commercial sources of each of the constituents of fertilizers are as follows:

1. **Nitrogenous matter.** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, and cyanamide; also nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and, especially, animal excrements.

2. **Phosphates.** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source, however, is entirely inadequate, and the great



FIG. 206. Mining phosphate rock in Florida

supply comes from the rock phosphates, which contain about 70 per cent calcium phosphate. These rock phosphates are quarried in large quantities, especially in Florida (Fig. 206) and Tennessee. Since calcium phosphate is nearly insoluble, the rock is ground and then treated with sulfuric acid. This converts the insoluble calcium phosphate into the soluble calcium acid phosphate ($\text{CaH}_4(\text{PO}_4)_2$):



The calcium sulfate also adds to the value of the fertilizer, furnishing sulfur and improving the physical qualities of the soil. Certain products (slags) formed in the manufacture of steel contain phosphorus and are also used in fertilizers.

3. *Potassium compounds.* These are obtained principally from the natural deposits in Germany and France (Fig. 184). Wood ashes are excellent, but the supply is limited.

Commercial fertilizers. As a rule the fertilizers on the market are mixtures of the three fundamental materials referred to above. The composition is varied according to the crop to be grown as well as to the nature of the soil; for example, potatoes demand a fertilizer rich in potassium, while



FIG. 207. The effect of fertilizers upon the growth of plants

a cereal, such as wheat, is benefited more by one rich in phosphates. Instead of using a fertilizer containing all three constituents, it is preferable to find out by experiment just what plant food is lacking in individual soils and then to make a proper mixture of such fertilizing materials as will furnish the desired food. Fig. 207 shows the result of such an experiment. Pot 1 shows the

result obtained with no fertilizer, pot 2 the effect of one combination, and pot 3 that of another.

Utilization of atmospheric nitrogen. It has been pointed out that with few exceptions plants have not the power of assimilating free nitrogen (p. 79). Moreover, it is inevitable that the supplies of sodium nitrate and ammonium sulfate, which are now the chief nitrogenous products used in the manufacture of commercial fertilizers, will sooner or later become exhausted. It has been found possible to utilize the inexhaustible supply of nitrogen in the atmosphere by converting the nitrogen into compounds which contain the element in a form available for plant food. We have already discussed these methods (pp. 169, 334).

EXERCISES

1. Give examples of soil formation that have come under your observation.

2. Have you ever seen any evidence that the roots of plants and trees exert a strong mechanical pressure?

3. (a) Suppose the crops grown on a soil were not removed. What result would this have on the fertility of the soil? (b) Would the results be influenced by the nature of the crop?

4. Give two different methods for changing the nitrogen of the air into fertilizers.

5. Suggest a possible way of utilizing the large plant built at Muscle Shoals (p. 335) during the war for the manufacture of explosives.

6. What kind of crops enrich the soil (p. 79)?

7. What compound is present in wood ashes that makes the ashes a valuable fertilizer?

8. Would wood ashes, if available, be effective to "sweeten" soils?

9. Would air-slaked lime (p. 331) serve to sweeten soils?

10. Ground bones are sometimes used as fertilizers, but their action is slow. Explain.

11. How could you find out what mineral products are withdrawn from the soil by different kinds of crops?

12. In making fertilizers the sulfuric acid used contains about 50 per cent of hydrogen sulfate. What weight of such an acid is necessary for the treatment of 1 ton of rock phosphate containing 70 per cent of calcium phosphate?

CHAPTER XXXVIII

THE MAGNESIUM FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	OXIDE
Magnesium . . .	Mg	24.32	1.74	651°	920°	MgO
Zinc	Zn	65.37	7.10	419.4°	950°	ZnO
Cadmium . . .	Cd	112.4	8.64	320.9°	778°	CdO

The family. In the magnesium family are included the four elements magnesium, zinc, cadmium, and mercury. Between the first three of these metals there is a close family resemblance. In some respects mercury resembles copper more closely and will be studied in connection with that metal.

MAGNESIUM

General. Magnesium is one of the abundant elements, although it never occurs native. Like sodium and calcium it is obtained pure by the electrolysis of its compounds, the mineral *carnallite* (p. 311) being used for this purpose. The pure metal is silver white and so light that it will just sink in water. Air tarnishes it somewhat. The common acids readily dissolve it. When it is ignited it burns with great brilliancy, even in air, and gives a light rich in the rays which act upon photographic plates; *hence its use for making flash lights and fireworks and for the flares used in lighting battlefields at night.* Ordinary flash-light powder is a mixture of powdered magnesium and potassium chlorate or some similar oxidizing agent. Magnesium is also used in making alloys.

Occurrence. The most common forms of rocks containing magnesium are *dolomite* ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and *magnesite* (MgCO_3). *Asbestos*, *talc*, and *serpentine* are silicates of magnesium.

Magnesium oxide (MgO). This is the soft white powder often known as *magnesia*. It resembles lime in many respects, but is even more infusible; hence its use for making fire brick for lining furnaces. It combines with water to form the hydroxide $\text{Mg}(\text{OH})_2$, which resembles calcium hydroxide.

Magnesium chloride. Magnesium chloride occurs in many natural waters along with the chlorides of sodium and calcium. It is coming into use for making floors. A common floor covering is made by adding magnesium chloride to a mixture of wood fiber or asbestos and magnesium oxide. With the proper amount of water this mixture *sets*, forming a tough, somewhat elastic mass.

Magnesium carbonate (MgCO_3). The pure carbonate occurs as *magnesite*. More often it is associated with calcium carbonate to form *dolomite* or *dolomitic limestone*, which forms whole mountain ranges and strata in the earth's crust. Water containing carbon dioxide acts upon magnesium carbonate; just as it acts upon calcium carbonate (p. 328).

Magnesium sulfate (MgSO_4). Magnesium sulfate differs from calcium sulfate in that it is very soluble in water. It occurs in some springs and crystallizes in the form $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$. This hydrate is used in medicine under the name of *Epsom salt*. Large beds of the hydrate occur in Wyoming and Washington. It has a number of commercial uses, especially in the dye industry.

Magnesium silicates. *Asbestos* ($\text{CaMg}_3(\text{SiO}_4)_2$) occurs in quantities in the province of Quebec, Canada, and is used for making fireproof shingles, board, and for covering pipes to diminish heat radiation. *Talc* ($\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$), also known as *soapstone*, is valuable for making sinks and table tops and,

in finely ground form (*French chalk*), for toilet powders. *Serpentine* is a greenish silicate of some use as a building stone, while *meerschauum*, also a silicate, is used for pipe bowls and similar articles.

Boiler scale. When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material called *scale* deposits in the boiler. The formation of this scale may be due to several distinct causes:

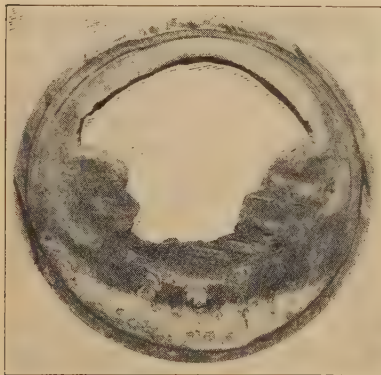


FIG. 208. Cross section of a boiler tube showing the deposit of boiler scale

1. **To the deposit of calcium sulfate.** This salt, although sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently, when water containing it is heated in a boiler the calcium sulfate precipitates and forms a hard scale.

2. **To decomposition of acid carbonates.** As we have seen, calcium and magnesium acid

carbonates are decomposed on heating, forming insoluble normal carbonates:



3. **To hydrolysis of magnesium salts.** Magnesium chloride and, to some extent, magnesium sulfate undergo hydrolysis when superheated in solution, and the magnesium hydroxide, being sparingly soluble, precipitates:



This scale adheres tightly to the boiler tubes in compact layers (Fig. 208) and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and its resistance to reagents. Thick scale sometimes cracks, and the water coming in contact with the overheated iron occasions an explosion.

ZINC

Properties. Zinc is the first of the metals so far studied that is familiar to all of us. It is a bluish-white metal, about as heavy as iron. If heated strongly in the air it takes fire and burns to the oxide ZnO . If the metal is melted and allowed to cool, it crystallizes and at ordinary temperature is quite hard and brittle; but if heated to between 100° and 150° it becomes malleable and can be rolled into thin sheets, and in this form the metal retains its softness and malleability at ordinary temperatures. When melted and poured into water it forms thin, brittle flakes known as *granulated* or *mossy* zinc; it is this form which is used in preparing hydrogen. Air tarnishes it but exerts no further action. It dissolves in all the common acids.

When the metal is quite pure, sulfuric and hydrochloric acids act upon it very slowly; when, however, it contains small amounts of other metals, such as magnesium or copper, or when it is merely in contact with another metal, brisk action takes place and hydrogen is evolved. For this reason, when pure zinc is used in the preparation of hydrogen a few drops of copper sulfate are often added to the solution to assist the chemical action.

Occurrence and metallurgy. Zinc does not occur free in nature, neither is it a constituent of common rocks. Its chief ores are the following: *sphalerite* (ZnS), *zincite* (ZnO), *smithsonite* (ZnCO_3), and *franklinite* ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$). The chief zinc-producing states are Missouri, Montana, and New Jersey.

To obtain the metal the ore is first roasted in the air, whereby the zinc in the ore is changed into the oxide. The oxide is then heated with carbon, which unites with the oxygen, liberating the zinc. The details of the process vary with the composition of the ore. Commercial zinc is often impure and contains small percentages of carbon, arsenic, and iron.

Uses of zinc. The chief use of zinc is in the manufacture of *galvanized iron*. This consists of sheets of iron covered with a thin layer of zinc, which protects the iron from rusting. About two thirds of all the zinc produced is used in this way. Sheet zinc is used as a lining for sinks and water-containers. Large quantities of the metal are used in making brass and other



FIG. 209. The manufacture of galvanized sheet iron

alloys (p. 282), in the construction of electrical batteries, and in separating silver from lead. In the laboratory it is used in the preparation of hydrogen and, in the form of zinc dust, as a reducing agent.

Manufacture of galvanized iron. Fig. 209 shows the method used in making galvanized iron. The plates of iron pass under the rollers at *A* and on into the pot of melted zinc *B*. The zinc adheres to the iron, and the resulting plate is passed under the roller *C* to remove the excess of zinc and to render the surface smooth. Sometimes the zinc is deposited on the iron by electrolytic methods.

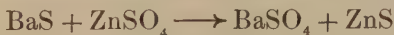
Compounds of zinc. In general the compounds of zinc resemble those of magnesium in formula and appearance, although they differ markedly in chemical conduct. The most important of them are listed below:

Zinc oxide (ZnO). This oxide occurs in impure state in nature. Commercially it is generally made by burning the metal in air. It is a pure-white powder which, under the name of *zinc white*, is much used as a white pigment in paints. It has an advantage over white lead in that *it is not changed in color by sulfur compounds* (which are likely to be present in the air of manufacturing districts), while lead compounds turn black. Many thousand tons of zinc oxide are used in paints each year. It is also used as a filler in the manufacture of rubber goods, especially automobile tires.

Zinc sulfate (ZnSO_4). This salt is readily crystallized from concentrated solutions in transparent colorless crystals which have the formula $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ and are called *white vitriol*. It is used in dyeing and in medicine.

Zinc chloride (ZnCl_2). This salt is very soluble in water and has a strongly acid reaction. It destroys the micro-organisms that cause decay and is used to preserve railroad ties and other wooden timbers especially subject to decay.

Zinc sulfide (ZnS). Very large deposits of zinc sulfide occur in southwestern Missouri, constituting the mineral *sphalerite*. *It is insoluble in water and, when pure, is white. Lithopone* is a mixture of the two solids barium sulfate and zinc sulfide, made by bringing together barium sulfide and zinc sulfate in solution:



It is a valuable white-paint pigment.

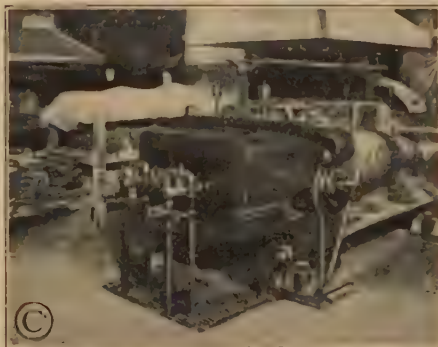
Preservation of wood. With the rapid disappearance of the forests the preservation of wood from decay (fungous growths) becomes a very important problem. When the wood is to be exposed merely to atmospheric conditions, it is preserved by paints



The rubber is obtained from rubber trees by tapping. The rubber, in the form of an emulsion, flows from the trees and is collected in buckets, as shown in A. This emulsion resembles milk in appearance and is known as the *latex*



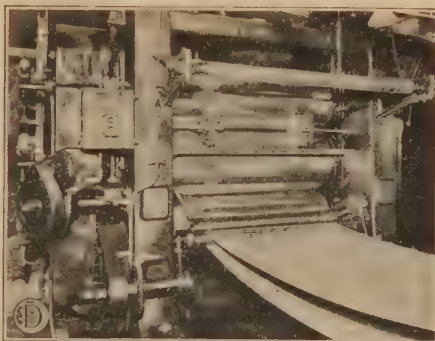
The rubber is obtained from the emulsion by adding acetic acid, or by pouring the emulsion, a little at a time, over the end of a stick and evaporating the water over a fire, as shown in B



The raw rubber is next mixed (or compounded) with sulfur and certain substances as zinc oxide and carbon black. This is done by running the materials between large revolving cylinders (O), as shown in C, until thoroughly mixed. Piles of the raw rubber are shown, marked n

FIG. 210, A, B, and C. Some steps in the manufacture of automobile casings

In D cotton fabric is being impregnated with the compounded rubber by running the fabric and rubber between large metal cylinders. In cord tires the cord is wrapped about the core and the cord as well as the interstices filled with rubber



As shown in E, the casing is then built up by winding the rubberized fabric on an iron wheel, the surface of which is the exact shape of the inner part of the desired casing. The details cannot be shown



The casing is then placed in a mold, as shown in F, and heated in large steam ovens. In this process the rubber is vulcanized and toughened. It is then removed and the finishing touches given it



FIG. 210, D, E, and F. Some steps in the manufacture of automobile casings

and varnishes. When it must be partly buried in the ground (railway ties, fence and telegraph posts), it is treated with substances that prevent decay. Those most frequently used are zinc chloride, copper sulfate, and creosote from coal tar.

Cadmium. This element very closely resembles zinc in most respects. Some of its alloys are characterized by having low melting points. Its compounds are similar in composition to the corresponding ones of magnesium and zinc.

RUBBER

Production. The statement has been made (pp. 109, 349) that carbonblack and zinc oxide are largely used in making certain rubber goods, and this suggests a brief discussion of rubber itself and its application in the making of some important rubber article, such as the casing of an automobile tire.

Rubber is the product of the rubber tree, which grows wild in the upper Amazon region and is cultivated in large numbers in tropical regions such as Java, Sumatra, Ceylon, and the Malay states. The percentage of rubber obtained from the cultivated trees has increased very rapidly as the demand for rubber increased; in 1900 only a very small fraction of 1 per cent was obtained from this source, while at present nearly 90 per cent of the world's output of rubber comes from the rubber plantations. The rubber is obtained from the trees by tapping (cutting through the bark), as shown in Fig. 210 A. An emulsion runs out and is collected in buckets. This fluid consists of water in which the rubber particles are suspended, much as the casein and fat are suspended in fresh milk; and just as the casein of milk can be coagulated by the addition of the acid, so the rubber particles can be coagulated by adding acetic acid (p. 295). An older method, still in limited use, consists in removing the water by evaporation, leaving the rubber. To do this, the emulsion (*latex*) is poured over the end of a stick which is then revolved over the hot smoke from a fire (Fig. 210 B). When the water evaporates the process is repeated until finally a ball of rubber is built up.

Composition. Pure rubber is a hydrocarbon whose molecular formula is some multiple of the simple formula C_5H_8 . It can be

made in the laboratory, but the process as yet developed is so costly that the synthetic rubber cannot compete with the natural product. Nevertheless, during the World War the Germans, shut off from natural supplies, made a considerable quantity of it and even equipped a few automobiles with tires made of synthetic rubber.

Vulcanizing rubber. The natural rubber is sticky and easily affected by the temperature, and as a result is worthless for most purposes. In 1839 Goodyear found that if the rubber is heated with sulfur these objectionable qualities are overcome. This process is known as *vulcanization*.

Compounding rubber. For most purposes the pure rubber is mixed or compounded with other materials, commonly known as *fillers*. These fillers impart strength or some other desired property to the finished product. Carbonblack and zinc oxide are the most common of these fillers. The color of a rubber article is often due to the filler used. Thus the red color of certain tires is due to the use of sulfide of antimony or oxide of iron, while the black color of other tires is due to carbonblack.

EXERCISES

1. (a) Name the metals so far studied. (b) How many of them will displace hydrogen from acids (p. 161)?
2. What is the difference in composition between limestone and dolomitic limestone?
3. Write the equation for the reaction (a) between magnesium and hydrochloric acid; (b) between magnesium and dilute sulfuric acid.
4. What reaction would take place if you added a solution of barium chloride to a solution of magnesium sulfate?
5. (a) Which of the metals so far studied is the heaviest? (b) Which has the highest melting point?
6. What is the difference in composition (a) between Glauber's salt and Epsom salt; (b) between magnesite and Iceland spar?
7. Water containing carbonic acid dissolves magnesite just as it dissolves limestone. What compound is formed in each case?
8. Suppose you had a supply of zinc and wished to prepare from it the compounds (a) zinc oxide, (b) zinc chloride, (c) zinc sulfide. Give the method you would use.

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Properties. Aluminium has many desirable properties. It is a silver-white metal, only about one third as heavy as iron, and yet it is malleable and ductile and fairly hard and strong. Moreover, it is an excellent conductor of heat and electricity.

Occurrence. Next to oxygen and silicon, aluminium is the most abundant of all the elements. The free element is not found in nature, but its compounds are widely distributed. The feldspars, which are the most abundant of all the minerals in the earth's crust, are all silicates of aluminium and either sodium, potassium, or calcium. Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminium, chiefly in the form of clay. Some of the other forms in which aluminium occurs in nature are the following: *corundum* (Al_2O_3); *emery* (Al_2O_3 colored black with oxide of iron); *cryolite* (Na_3AlF_6); *bauxite*, a mixture of hydrated aluminium oxides ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$) together with similar compounds of iron. Bauxite is the ore from which aluminium is prepared. In the United States it is found chiefly in Arkansas.

Preparation. The Hall process consists in the electrolysis of a solution of aluminium oxide (Al_2O_3) in melted cryolite.

An iron box *A* (Fig. 212) is connected with a powerful electrical generator in such a way as to serve as the cathode upon which the aluminium is deposited. Three or four rows of carbon rods *B*, *B* dip into the box and serve as the anodes. The box is partly filled with cryolite, and the current is turned on, generating enough heat to melt the cryolite. Aluminium oxide obtained from bauxite is then added, and acts as an electrolyte, being decomposed into aluminium and oxygen. The temperature is maintained above the melting point of aluminium, and the liquid metal, being heavier than cryolite, collects on the bottom of the vessel, from which it is tapped off from time to time through the tap hole *C*.

It will be noted that the rather rare mineral *bauxite*, and not the very abundant clay, is used as the source of aluminium.

No one has yet succeeded in finding an economical way of separating the metal from clay. Here is an opportunity for someone to make a discovery equal to that made by Hall.

Chemical conduct. Neither air nor boiling water has any marked effect upon the metal. When heated in oxygen it burns with great heat evolution; hence it is a good reducing agent. It dissolves readily in hydrochloric acid and hot

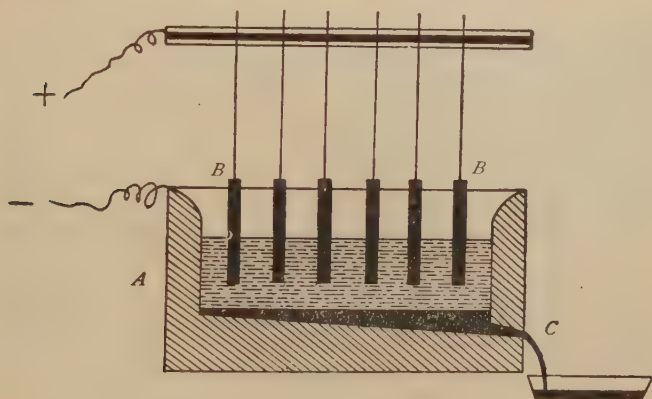


FIG. 212. Diagram illustrating the manufacture of aluminium

concentrated sulfuric acid, but nitric acid has little action upon it. *It is readily dissolved by alkalies and corroded by salt water.*

Uses. The lightness and strength of aluminium, together with its inactivity toward air and water, suggest many uses. About one third of the output is used in making automobiles. Large amounts are also used in the steel industry. Its use in the manufacture of kitchen vessels of all kinds is well known. Owing to its electrical conductivity it is replacing copper to some extent, especially for trolley and power wires. In the form of a powder suspended in a suitable liquid it makes an efficient, silver-like paint. Many desirable alloys of aluminium have been prepared: *aluminium bronze* (90 per cent

copper and 10 per cent aluminium) has a gold-like color, and is strong and permanent in the air. *Duraluminum* and *magnalium* are also important alloys.

The World War developed many new uses for aluminium. For example, it constituted about one third of the weight of the Liberty motor. It was also used in constructing aëroplanes and dirigible balloons (Fig. 7). The powdered metal was used in certain bombs and explosives.

Goldschmidt reduction process. Aluminium is frequently employed as a powerful reducing agent, many metallic oxides which resist reduction by carbon being readily reduced by it.

The aluminium, in the form of a fine powder, is mixed with the metallic oxide, together with some substance such as fluorite, which melts and thus assists by bringing the reacting compounds in close contact. The mixture is ignited, and the aluminium unites with the oxygen of the metallic oxide, liberating the metal. This collects in a fused condition under the melted fluorite.

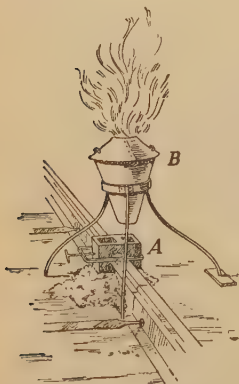


FIG. 213. Welding car rails with thermite

Thermite welding process. The property possessed by aluminium, of reducing oxides with the liberation of a large amount of heat, is turned into practical account in

the welding of metals,—a method devised by the German chemist Goldschmidt. This method may be illustrated by a single example, namely, the welding of car rails,—a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 213) is then clamped about the ends of the rail, leaving sufficient space so that the metal can flow in. The ends of the rails are heated to redness by the flame from a gasoline torch directed into the opening in the mold. Just

over the opening is placed the crucible *B*, which contains a mixture of iron, metallic oxides, and aluminium. When the ends of the rails have been heated to redness by the torch, the mixture in the crucible is ignited, and after a few seconds the crucible is opened at the bottom, and the molten metal resulting from the reaction is allowed to flow into the mold. In this way the molten metal surrounds the ends of the rails and, as it cools, joins them firmly together. A mixture of the metallic oxides and aluminium ready for use in welding is sold under the name of *thermite*.

The largest weld ever made was that of the sternpost of the army transport *Northern Pacific*, which was broken during the World War when the ship ran aground in a fog off Long Island (Fig. 214).



FIG. 214. View of the stern of the *Northern Pacific* showing the broken post after being welded by thermite (the break is at the point indicated by the arrow)

Aluminium oxide (Al_2O_3). This substance occurs in several forms in nature. The relatively pure crystals are called *corundum*; *emery* is a variety colored dark gray or black, usually by iron compounds. In transparent crystals, tinted different colors by traces of impurities, it forms such precious stones as *sapphire*, *ruby*, *topaz*, and *oriental amethyst*. All these varieties are very hard, falling little short of the diamond in this respect. The cheaper forms, corundum and emery, are used for cutting and grinding purposes. Chemically pure aluminium oxide can be made by igniting the hydroxide. The oxide so prepared is used in the preparation of aluminium. Some laboratory

utensils, such as crucibles and tubes, are made of aluminium oxide, which is given the trade name *alundum*. The same material is used for cutting and polishing metals.

Artificial gems. A number of gems are now prepared in the laboratory from molten aluminium oxide. The white sapphires so extensively advertised are simply the pure oxide. By fusing the aluminium oxide with small percentages of certain other



FIG. 215. A row of furnaces used in making artificial rubies
Oxygen is used to obtain high temperatures

metallic oxides (Fig. 215), different tints or colors are obtained, and in this way are prepared such gems as the ruby, the oriental amethyst, and the yellow and blue sapphires, which are practically identical in composition and properties with the natural stones.

Aluminium hydroxide ($\text{Al}(\text{OH})_3$). The hydroxide can be prepared by adding ammonium hydroxide to any soluble aluminium salt, forming a colloidal precipitate which is insoluble in water but very hard to filter.

Water purification. The value of aluminium hydroxide in the purification of water (p. 66) is due largely to its colloidal or gelatinous character when freshly formed by precipitation. After being stirred through the water it is allowed to settle slowly, and in so doing it carries with it any suspended matter present, including microorganisms and coloring materials. Instead of adding aluminium hydroxide itself to the water, it is more economical and effective to produce it by precipitation. This is done by dissolving in the water some cheap salt which readily hydrolyzes, such as aluminium sulfate:

$$\text{Al}_2(\text{SO}_4)_3 + 6 \text{H}_2\text{O} \longrightarrow 2 \text{Al}(\text{OH})_3 + 3 \text{H}_2\text{SO}_4$$

There is always sufficient basic material present in the water to combine with the sulfuric acid set free, so that no acid is left in the water as a result of this treatment.

Fig. 216 illustrates the use of aluminium sulfate in purifying water. The cylinder *A* contains impure water. *B* is a cylinder of the same impure water to which some aluminium sulfate has been added. The aluminium hydroxide formed by hydrolysis is slowly settling in the water, carrying with it the impurities. The appearance of the water after settling is shown in *C*.

Some cities both purify and soften the entire city water-supply. In Columbus, Ohio, for example, as high as 40,000,000 gallons is treated daily. The compounds used are (1) aluminium sulfate to purify the water, and (2) calcium oxide and sodium carbonate (p. 329) to soften it. These compounds are mixed and thoroughly stirred through the water (Fig. 194). A heavy, flocculent precipitate forms. The water then runs into settling basins (Fig. 217; notice the white solid matter in the water as it enters). Here it flows slowly forward and backward between walls until the precipitate settles. The water is then drawn off, treated with chlorine (p. 141), and filtered.

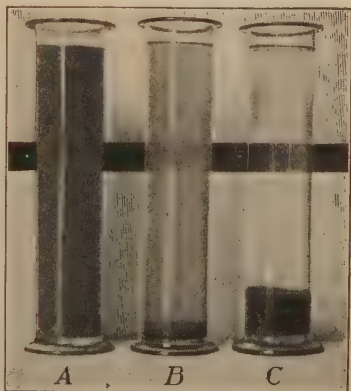
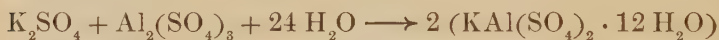


FIG. 216. Purification of water by aluminium sulfate

Alums. Aluminium sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation



The sulfates of other trivalent metals can form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminium. They all crystallize in eight-sided crystals and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:



Very large, well-formed crystals of an alum can be prepared by suspending a small crystal by a thread in a saturated solution of

the alum, as shown in Fig. 218. The small crystal slowly grows and assumes a very perfect form.

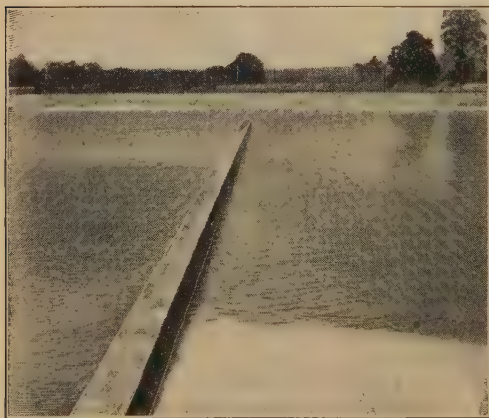


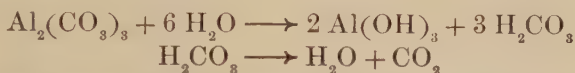
FIG. 217. Settling basin used in water purification

Hydrolysis of salts of aluminium. While aluminium hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydro-

lyzed (p. 308). Thus, when an aluminium salt and a soluble carbonate are brought together in solution, we should expect to have aluminium carbonate precipitated according to the equation



But if it is formed at all, it instantly begins to hydrolyze, the products of the hydrolysis being aluminium hydroxide and carbonic acid:



Aërating agents used in baking. In preparing foods made largely from dough, such as bread, biscuits, and cake, it is essential that some *aërating agent* be used to render the food light and wholesome. The aërating agent used in all cases is carbon dioxide. This is generated in the dough and, pushing its way through the mass, renders it porous and light. The following methods are used for generating the gas in baking:

1. *By alcoholic fermentation.* As we have seen, this is the method generally used in making bread (p. 256).

2. *By the action of sour milk on sodium bicarbonate.* The lactic acid present in the sour milk (p. 241) slowly acts upon the bicarbonate, liberating carbon dioxide:



3. *By the action of an acid salt or alum upon sodium bicarbonate; baking powders.* Every baking powder contains three ingredients, the name and function of each of which is as follows: (1) sodium bicarbonate to furnish the carbon dioxide; (2) some compound which in the presence of water reacts with the bicarbonate and slowly liberates carbon dioxide; and (3) starch or flour, which keeps the powder dry by absorbing moisture and hence prevents deterioration. The compounds used for liberating the carbon dioxide from the bicarbonate are either cream of tartar, calcium acid phosphate, sodium acid phosphate, or alum. A baking powder is generally designated by the name of the compound used to liberate the carbon dioxide. Thus, we speak of cream of tartar baking powders or alum baking powders.

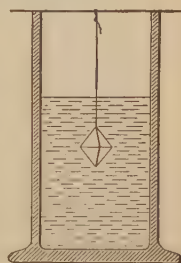
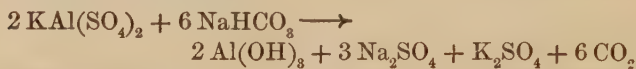


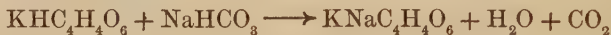
FIG. 218. Growing a perfect crystal of alum

Reactions of baking powders. The reactions that take place when water is added to each of the classes of baking powders are represented in the following equations:

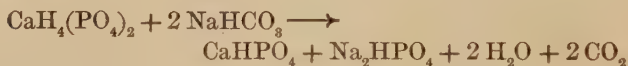
Alum (supposing that the alum present is potassium alum):



Cream of tartar:



Phosphate:



DYES AND DYEING

Properties of dyes. We have already learned (p. 235) something of the aniline dyes and the history of their discovery. Because of their very great coloring power these dyes have almost entirely taken the place of the dyes extracted from plants and trees (Fig. 219).

The requisites of a good dye are as follows: (1) it must have an acceptable color; (2) it must not injure the fabrics; (3) it must *dye fast* (in other words, the cloth after having been dyed must retain its color when washed with water); (4) it must not fade too easily.

The process of dyeing. This process consists in fixing the dye uniformly upon the fabric. The animal fibers, namely, wool and silk, are as a rule more readily dyed than cotton, which is a vegetable fiber. To dye wool and silk with most dyes it is only necessary to steep the fabric in a solution of the dye. Cotton fabrics, when treated in this way, will become colored, but with most dyes the color is not *fast*. Cotton fabrics may be dyed fast in the following way:

The cloth is first soaked in a solution of an aluminium salt (or a similar substance), which readily undergoes



Iron

Chromium

Tin

Aluminium

THE USE OF MORDANTS IN DYEING

The central panel in the figure represents a piece of white cotton cloth. A mordant of iron, of chromium, of tin, and of aluminium has been applied to the cloth in four vertical stripes (leaving the spaces between without a mordant). The upper panel shows the same cloth after being dyed with gallein; the lower panel shows a similar piece of cloth after being dyed with alizarin

hydrolysis. The cloth is then exposed to the action of steam, which hydrolyzes the salt, leaving the gelatin-like hydroxide thoroughly incorporated in the fiber. The cloth is then steeped in the dye, which is absorbed by the aluminium hydroxide and is in consequence fastened, or "fixed," upon the fiber.



FIG. 219. Interior of an indigo factory

Indigo, one of our most common dyes, was formerly obtained from a plant grown largely in India. Now it is made from coal tar (benzene) at a lower cost

Aluminium hydroxide and other substances which act in the same way are called *mordants*. The same dye will often give different colors with different mordants, as shown upon the accompanying colored plate.

Lakes. The compounds which serve well as mordants may be precipitated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes* and are used as pigments in paints.

EXERCISES

1. State the valences of the metals so far studied.
2. Enumerate the metals and compounds so far studied that are prepared by electrolysis.
3. Aluminium has been termed the "ideal metal." Give reasons for such a claim.
4. (a) Name the four most abundant elements in the order of their abundance (p. 9). (b) Which is the more abundant, iron or aluminium?
5. Mention two important chemical discoveries made by young men.
6. Write the equation for the reaction which takes place when aluminium dissolves in hydrochloric acid.
7. Why do the directions for using aluminium cooking utensils state that such utensils should not be washed in strong soaps?
8. Where should you expect factories for the production of aluminium to be located?
9. What substance has largely taken the place of emery for cutting and grinding purposes?
10. (a) What is the aërating agent used in making bread? (b) Why not use baking powder?
11. When baking soda is heated, carbon dioxide is evolved (p. 308). Why not use it alone as an aërating agent?
12. Why does bread have to be set aside to "raise," while biscuits and cakes do not?
13. Since the passage of the prohibition act cream of tartar baking powders are not made in such large quantities. What is the relation between prohibition and baking powders?
14. What compounds remain in foods as a result of the use of the different kinds of baking powders?
15. Do you think that a mixture of baking soda and lemon juice would act as an aërating agent?
16. Would baking soda and sweet milk serve as an aërating agent?
17. Would you classify indigo as a vegetable dye or as a coal-tar dye?
18. An aluminium plant has an output of 2 tons daily. What weight of aluminium oxide (Al_2O_3) would be required daily in the plant?

19. Which contains the greater percentage of water of hydration: potassium alum or borax?

20. (a) What is the relation between the number of gram-molecular weights of baking soda used in a baking powder and the number of gram-molecular weights of carbon dioxide generated (see equations, p. 362)? (b) Calculate the volume of carbon dioxide generated by 10 g. of baking soda present in a baking powder.

21. In what proportion should cream of tartar and baking soda be mixed in a baking powder (see equation, p. 362)?

22. Ordinary baking powders contain about 12 per cent of starch or flour. Calculate the weights of cream of tartar, baking soda, and starch required to make 100 g. of cream of tartar baking powder.

23. (a) Six grams (approximately 2 level teaspoonfuls) of the baking powder of the composition referred to in exercise 22 would evolve what weight of carbon dioxide? (b) The Federal law requires that a baking powder sold on the market must generate 12 per cent of its weight of carbon dioxide. Would the baking powder in exercise 22 meet these requirements?

CHAPTER XL

SILICATES AND THEIR COMMERCIAL APPLICATIONS

Introduction. There are a number of industries in which the raw materials used are sand, clay, limestone, and feldspar. In the process of manufacture these ingredients form complex silicates, so that it is convenient to discuss these industries

under the general term of *the silicate industries*. The most important of these industries are those of *glass, cement, and clay products*, including such objects as brick, pottery, and chinaware.



FIG. 220. Making a glass object in a mold

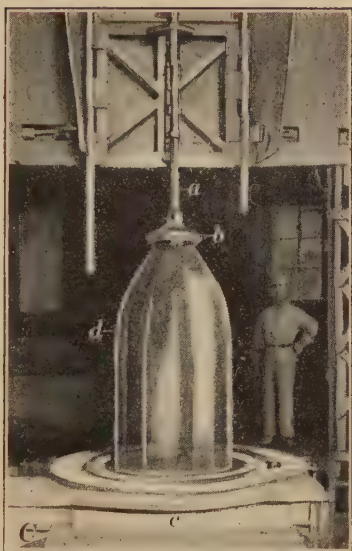
Glass. When certain silicates (such as those of sodium, potassium, and calcium) are heated together to a

high temperature with silicon dioxide (sand), the mixture slowly fuses to a transparent liquid, which, on cooling, passes into the rigid material called *glass*. In its real nature glass is to be regarded as a supercooled liquid rather than as a true solid. Instead of starting with the silicates of sodium and calcium, it is more convenient and economical to heat sodium carbonate (or sulfate) and lime with an excess of clean sand, the silicates being formed during the heating:





The older method



The newer method

FIG. 221. The manufacture of window glass

In making window glass, the glass is first formed into cylinders. In the old process, still in use, the cylinder is blown into shape by skilled glass-blowers. The glass-blower first collects, on the end of a hollow rod, a mass of molten glass in the form of a ball (*A*, Fig. 221); then by using great skill, swinging the soft glass backwards and forwards (*B*) to prevent the glass from sagging, and at the same time blowing through the rod, the glass is blown into the form of a large cylinder five or six feet in length and one or two feet in diameter. The comparatively expensive method of blowing the cylinder by mouth is giving way to the machine-blown methods, the principle of which is as follows: A long hollow rod (*C*, *a*) with a flattened end (*c*, *b*) is lowered until the end is in contact with molten glass in a pot (*C*, *c*). Air is then forced through the rod and at the same time the rod is slowly raised. The molten glass clings to the end of the rod, and as the rod is raised the glass is formed into cylindrical shape by the air pressure from within and hardens as it is raised above the mass (*C*, *d*). This process makes it possible to form much larger cylinders than in the case of the mouth-blown method, some of the cylinders being as large as two feet in diameter and forty feet in length. The ends of the cylinder of glass formed by either of the above methods are removed and the open cylinder cracked lengthwise. The cracked cylinder is then placed on the flat hearth of a large furnace and slowly heated until soft. The cylinder then opens out in the form of a large glass plate, much as a cylinder of paper when cut lengthwise will open into a sheet of paper. The glass is allowed to cool slowly, and is finally cut into pieces of the desired size.



A



B



C



D

FIG. 222. The manufacture of a glass beaker

The glass-blower first collects the proper amount of molten glass on the end of a rod (*A*). This is then placed in the mold (*B*) and blown into shape (the workman in *B* is shown removing the beaker from the mold). The glass is then cut from the top of the beaker by revolving it in contact with a diamond (*C*). Finally, the beaker is heated until slightly soft, when the rim is formed, as shown in *D*

Molding and blowing glass. The way in which the melted mixture is handled in the glass factory depends upon the character of the object to be made. Many articles, such as bottles, are made by blowing the plastic glass into hollow molds of the desired shape. The mold is opened, a lump of plastic glass on a hollow rod is lowered into it, and the mold is then closed. By blowing into the tube the glass is forced into the shape of the mold. The mold is then opened (Fig. 220) and the object lifted out. The top of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now more often made by machinery, in which the bottle is blown by compressed air.

Other objects, such as lamp chimneys, glasses, and beakers, are revolved while being blown in the mold, and have no ridge showing where the mold closes. Window glass has long been made by blowing cylinders of glass as explained in Fig. 221. Similar cylinders are also made by dipping a tube into melted glass and slowly withdrawing it while compressed air is forced into the tube. Increasing amounts are also being made by allowing the molten glass to flow out onto tables under very definite conditions. Plate glass is cast into flat slabs, which are then ground and polished to perfectly plane surfaces.

Varieties of glass. By the proper selection of ingredients a great variety of glass can be made. Window glass and bottle glass are chiefly silicates of sodium and calcium. While we think of such glass as insoluble, nevertheless it will not serve for beakers in which strong chemicals are heated. For such objects some boric acid is used along with the sand, so that the resulting product is a *borosilicate* of the metals present. *Pyrex glass*, used to withstand shock and sudden changes of temperature, is a sodium-aluminium borosilicate containing a large percentage of free silica. Optical glass, imported from Germany before the war, but now made in the United States, owes its brilliancy to the presence of lead silicate.

Color of glass. The presence of small amounts of certain metals impart characteristic colors to glass. Thus, cobalt

compounds give a blue color, while manganese imparts an amethyst tinge. Gold produces the finest ruby color, while cuprous oxide and selenium give similar ruby tints. The sand used in glassmaking must be very pure; otherwise the iron present as an impurity will produce a green color observed in bottles made from cheap grades of sand. In some cases the color is due to the presence of a colored silicate formed by



FIG. 223. The manufacture of pottery: molding the plastic material into form

the metal used; in others, as in the case of gold, the color is due to the presence of the metal in the form of a colloid.

Aluminium silicates. When feldspar (KAlSi_3O_8) is decomposed, as explained in the chapter on soils (p. 338), there are formed soluble potassium compounds, which find their way into

the soil, and aluminium silicate, which is sometimes deposited in beds in nearly pure form known as *kaolinite* ($\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$); more often it is found mixed with sand and other substances, in which form it is known as *clay*. *Kaolinite, as well as a clay, when mixed with water, forms a plastic mass* which can be molded or fashioned into any desired shape, and this when baked forms a hard mass; hence their use in making bricks, pottery, and chinaware. *Fuller's earth* is a peculiar form of aluminium silicate which is used as a filtering material for decolorizing oils such as cottonseed oil.

Clay products. The crudest forms of clay products, such as porous brick and drintile, have little chemistry involved

in their manufacture. Natural clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless iron compounds in the clay are converted into colored compounds which give the usual red color to these articles.

In making *vitrified brick* the temperature is raised to the point at which fusion begins, so that the brick is partially changed to a kind of glass.

White pottery. This term is applied to a variety of articles, from the crudest porcelain to the finest chinaware. Although the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under

three heads; namely, (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

1. The body of the ware. The materials used consist of an artificially compounded clay made from kaolin, plastic clay, and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel (Fig. 223). The ware is then dried and burned in a kiln (Fig. 224) until vitrified, and in this form is known as *bisque*. This is usually porous and must therefore be glazed to render it nonabsorbent.

2. The glaze. The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are quartz, feldspar, and various metallic oxides, often mixed with a little



FIG. 224. The manufacture of pottery: stacking the ware in the kiln for firing

boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste. The bisque is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

3. *The decoration.* If the article is to be decorated the design may be painted upon the body before glazing, or it may be painted upon the glaze and the article fired again, the pigments melting



FIG. 225. A bridge built of reinforced concrete

into the glaze. In the former case the pigments used are as a rule metallic oxides of various colors, while in the latter case they are often colored glasses.

Cement. The term *cement* as ordinarily used at present is applied to those mortars which possess the property of *hardening in water as well as in air*. These cements are silicate bodies, usually very highly basic in character, and when ground fine and mixed with water they undergo complex reactions resulting in the formation of a hard, rocklike mass. A number of different classes of cements are known, the most important of which is called *Portland cement*.

Manufacture of Portland cement. The materials most commonly employed are limestone and clay or shale, although any products may be used which are similar in composition to the above materials.

The materials to be used are coarsely ground and then mixed together in the proper proportions and finely pulverized. The

resulting mixture is run into a furnace and burned to a temperature just short of fusion, at which temperature it vitrifies, forming a grayish mass known as *clinker*. Finally, the clinker is ground to a fine powder. Gypsum is often added in the process; this acts as a negative catalyzer, retarding the hardening, or setting, of the cement.

Importance of cement. The importance of cement in the construction industries increases each year. It is often used in place of mortar in the construction of brick buildings. Mixed with crushed stone and sand it forms *concrete*, which is used in foundation work for buildings, street-paving, and road-building. It is also used in making artificial stone, terra-cotta trimmings for buildings, artificial-stone walks and floors, fence posts, and the like. It is being used more and more for making articles which were formerly made of wood or stone, and ships and the entire walls of buildings are sometimes made of cement blocks or of concrete. Iron rods or wire are often embedded in the concrete before it sets, to give it greater strength, and this is called *reinforced concrete* (Fig. 225).

EXERCISES

1. Sodium silicate alone forms a hard transparent mass. Why not use this as glass?
2. What sort of glass would be produced if ordinary impure sand were used in place of white sand?
3. How can you easily show that window glass has a very pronounced color?
4. Why not make glass from sand alone?
5. What is the difference in composition between feldspar, kaolinite, and clay?
6. What properties have kaolinite and clay in common that makes them adapted for the manufacture of pottery?
7. Why is it necessary to glaze chinaware?
8. (a) What is the distinction between mortar and cement?
(b) Could cement be used for laying bricks?
9. Give examples of structures you have seen that are made of cement.
10. Is there any relation in properties between Fuller's earth and charcoal?

CHAPTER XLI

THE IRON FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	OXIDES
Iron	Fe	55.84	7.86	1530°	FeO, Fe ₂ O ₃
Cobalt	Co	58.97	8.60	1480°	CoO, Co ₂ O ₃
Nickel	Ni	58.68	8.90	1452°	NiO, Ni ₂ O ₃

The family. The elements iron, cobalt, and nickel form a group in the eighth column of the periodic table. The atomic weights of the three are very close together, and their properties are very much alike.

IRON

Introduction. Next to aluminium, iron is the most abundant of the metals. While it is not found free in nature (except in meteorites), nevertheless it has long been known and utilized. This is due to the fact that it is easy to separate from its ores, can be easily molded or hammered into shape, and possesses properties that make it useful for many purposes. There are many varieties of iron, the properties of which vary because of the method of manufacture and the presence of other elements, especially carbon. The properties of each of these will be described after their manufacture and composition have been studied.

Occurrence. Iron occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, very few rocks or soils are free from small

percentages of iron. It is a constituent of the chlorophyll of plants and the hæmoglobin of the blood of animals and therefore plays an important part in life processes. Many meteorites are largely iron in the free state, usually alloyed with a little nickel.

Pure iron. Iron can be prepared in practically pure condition by the open-hearth method (p. 379). It is a silvery metal which melts at 1530° . It is ductile and malleable and is almost as soft as aluminium. It is especially well adapted to the manufacture of electromagnets, since it acquires and loses magnetic properties more readily than do the ordinary varieties of iron. It is also used for purposes where resistance to corrosion is desired, for it does not rust rapidly.

Iron of commerce. Iron differs from most of the other metals used in the industries in that the pure metal is only prepared to a limited extent and is of limited application, while that containing small percentages of other elements exhibits a wide variety of properties which make it of the greatest value for many different purposes.

Carbon is always present in amounts which vary from a mere trace to about 7 per cent. According to the condition of treatment, the carbon may be in the form of graphite scattered through the iron, or it may occur dissolved in the iron, or as carbides of iron. One of the most important of the many carbides of iron is that which has the formula Fe_3C and is called *cementite*. Manganese, silicon, and traces of phosphorus and sulfur, together with a little oxygen, are also present.

The properties of the iron are greatly modified by the percentages of these elements, by their form of combination, and by the treatment of the metal during its production. The result is that we have many varieties of iron. The most common of these varieties recognized in commerce are the well-known forms termed *cast iron*, *wrought iron*, and *steel*.

Materials used in metallurgy of iron. Four different classes of materials are used in the metallurgy of iron :

1. **Iron ore.** The ores most frequently employed are the following :

Hematite	Fe_2O_3	Siderite	FeCO_3
Magnetite	Fe_3O_4	Limonite	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

While iron ore is mined in a number of different localities in the United States, the great center of production is in the



FIG. 226. Mining iron ore in Minnesota

neighborhood of Lake Superior, the ore being chiefly *hematite*. Large amounts are also mined near Birmingham, Alabama. Fig. 226 represents one of the large mines in Minnesota.

2. **Carbon.** Carbon in some form is necessary both as a *fuel* and as a *reducing agent*. In

former times wood charcoal was used to supply the carbon, but now coke is almost universally used.

3. **Hot air.** To maintain the high temperature required for the reduction of iron, a very active combustion of fuel is necessary. This is secured by forcing a strong blast of *hot air* into the lower part of the furnace during the reduction process.

4. **Flux.** All the materials which enter the furnace must leave it again, either in the form of gases or liquids. The *iron* is drawn off as the liquid metal after its reduction, the *oxygen* with which it was combined escaping as oxides of carbon. To secure the removal of the *earthy matter* charged into the furnace along with the ore, materials are added to the charge which will combine with the impurities in the ore,

forming a liquid. The material added for this purpose is called the *flux* and usually consists of limestone. The liquid produced from the flux and the ore is called *slag*. It is a variety of readily fusible glass.

Cast iron. Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron*. The ores are mixed with a suitable flux and are reduced by heating with coke.

Blast-furnace process. The reduction is carried out in a large tower called a *blast furnace* (Fig. 227). This is usually 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes *A*, called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe *B*, which girdles the furnace. At the base of the furnace is an opening through which the liquid metal can be drawn off from time to time. There is also a second opening *C*, somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap *D*, called the *cone*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through pipes *E*. These gases are very hot and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères and as fuel for the engines.

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the cone.

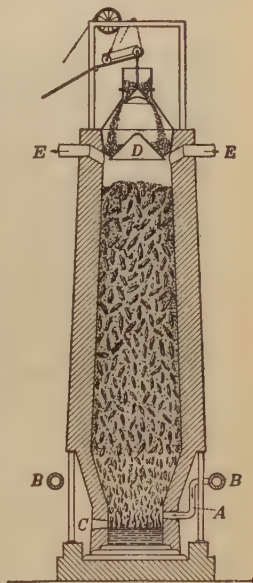


FIG. 227. Vertical section of a blast furnace

The coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends the reduction is completed, and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has

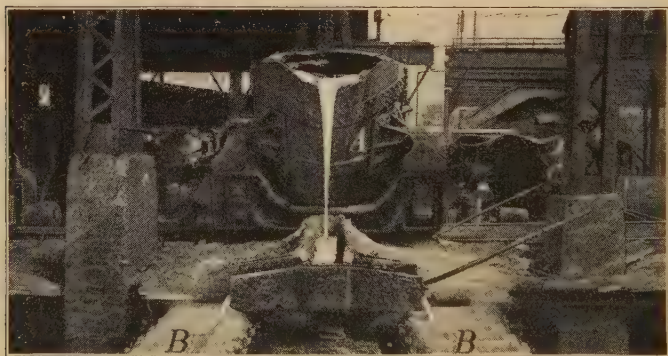


FIG. 228. Casting pig iron from a blast furnace

collected, the slag is drawn off through *C*. The molten iron is then run into large ladles or buckets (Fig. 228, *A*) and used directly in the manufacture of steel; or it is poured from the buckets into iron troughs (Fig. 228, *B, B*) or molds lined with lime. These troughs are attached so as to form an endless belt. The molten iron in each trough solidifies by the time it reaches the farthest point; and as the belt reverses, the solid pieces of iron fall into cars placed beneath it.

In practice a number of furnaces are usually operated together, as illustrated in Fig. 229, which shows an exterior view of a modern plant for making cast iron.

Properties of cast iron. The iron produced in the blast furnace is called *cast iron*. It varies considerably in composition, but always contains over 2 per cent of carbon, variable amounts

of silicon, and at least traces of phosphorus and sulfur. The form in which the carbon is present, whether free or combined, also greatly modifies the properties of the iron. In general, cast iron is hard and brittle and melts at about 1100° . It cannot be welded or forged, but is easily cast in sand molds.

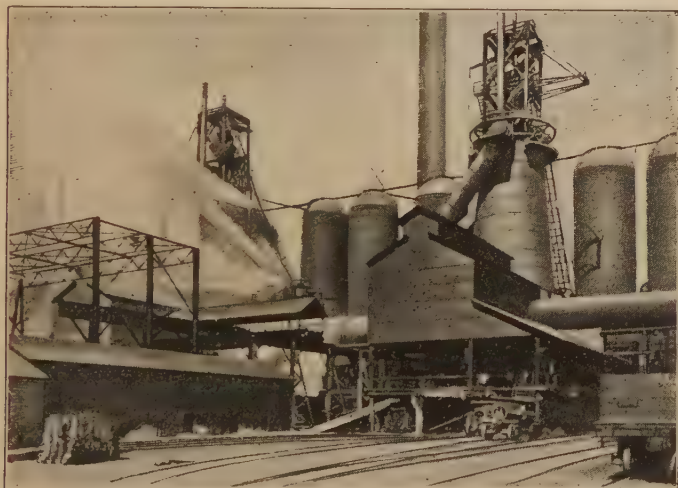


FIG. 229. A typical plant for the manufacture of cast iron

It is rigid, but not elastic, and its tensile strength is small. It is used for making castings, but chiefly as a starting point in the manufacture of other varieties of iron.

Wrought iron. Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur, the operation being conducted in what is called a *puddling furnace*.

Wrought iron is soft, malleable, and ductile. Its tensile strength is greater than that of cast iron, but less than that of most steel. Its melting point is much higher than that of cast iron. It is no longer produced to the same relative extent as in former years, since soft steel can be made at a less cost and has almost the same properties.

Steel. Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are quite different from that employed in the manufacture of wrought iron. Nearly all the steel of commerce produced in the United States is made by one of two general methods known as the *acid Bessemer process* and the *basic open-hearth process*.

Acid Bessemer process. In the acid Bessemer process the furnaces used are lined with *silica*, which, it will be recalled, is an *acid anhydride*. These furnaces remove from the cast iron the carbon and silicon, but not the phosphorus and sulfur. The process is therefore employed when the cast iron to be used is low in phosphorus and sulfur.



FIG. 230. Vertical section showing details of a Bessemer converter

Details of the Bessemer process. This process, invented about 1860, is carried out in great egg-shaped crucibles called *converters* (Fig. 230), each of which will hold as much as 15 tons of steel. The converter is built of steel and lined with silica. It is mounted on axles, or *trunnions*, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber *A*, which forms a false bottom to the converter. The true bottom is perforated so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

White-hot liquid cast iron from a blast furnace is run into the converter through its open, necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on and the converter turned to a nearly vertical position. The carbon and silicon in the iron are rapidly oxidized (first the silicon and then the carbon), the oxidation being attended by a brilliant flame (Fig. 231). The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued

until the character of the flame shows that all the carbon has been burned away. The process requires from fifteen to twenty minutes, and when it is complete the desired quantity of carbon (generally in the form of high carbon iron alloy) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects.

Basic open-hearth process. In the basic open-hearth process the lining of the furnace is made of limestone or dolomite, both of which act as *bases*. In such furnaces the phosphorus and sulfur are both removed, as well as the silicon and carbon. The presence of more than traces of phosphorus and sulfur in the finished steel renders the metal so brittle that



FIG. 231. The brilliant flame of a Bessemer converter

it is worthless. The open-hearth process therefore possesses a great advantage over the acid Bessemer process in that it makes it possible to utilize iron ores (or cast iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced. An average furnace produces about fifty tons of steel in one operation, approximately eight hours being required in the process.

In the open-hearth process cast iron is introduced into long, low furnaces (Fig 232) lined with limestone or dolomite and heated with a gas flame passing above and over the iron. The carbon present oxidizes and escapes. The silicon, phosphorus, and sulfur are oxidized, and the resulting oxides combine with some of the lime lining to form a slag which floats on the surface and is easily removed. When the operation is complete the liquid steel is drawn off (Fig. 233) into large buckets and then run into molds. Most of our steel is made by this process.

Electrothermal metallurgy of steel. An increasing quantity of high-grade tool steel is being produced in electrical furnaces. The electrical current is used merely to produce heat, so that the process is not dependent upon electrolysis. This method is almost identical with the open-hearth method, save in the way in which the heat is supplied, and produces the same kind of steel as does the latter method.

Properties of steel. Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, and not more than traces of phosphorus and sulfur. When desired, a product containing as high as 99.85 per cent of iron can be produced by the open-hearth method. Such steel is very soft, but resists rusting. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel can be rolled into sheets, cast in molds, and forged into desired shapes.

The hardening and tempering of steel. When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then allowed to cool slowly, this hardened steel becomes softer and less brittle, and this process is known as *tempering*.

By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any condition of hardness demanded for a given purpose, as for making springs

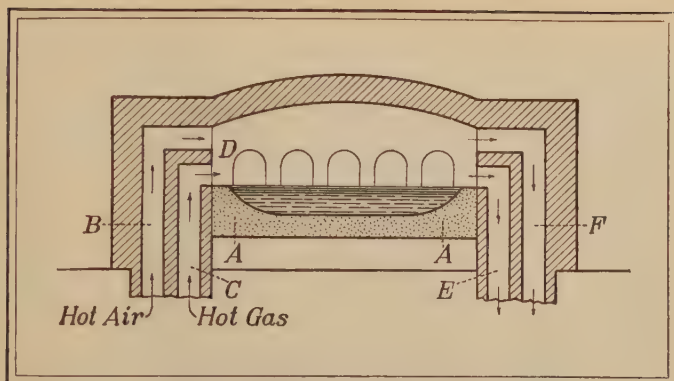


FIG. 232. Diagram of an open-hearth furnace

The fuel gas previously heated enters through *C*, and at *D* meets a current of hot air entering through *B*. Vigorous combustion ensues, and the flame passes over the cast iron in the furnace, melting it and gradually changing it into steel. The hot products of combustion escape through *E* and *F* and are used in heating the incoming supplies of gas and air. The limestone lining is shown at *A, A*

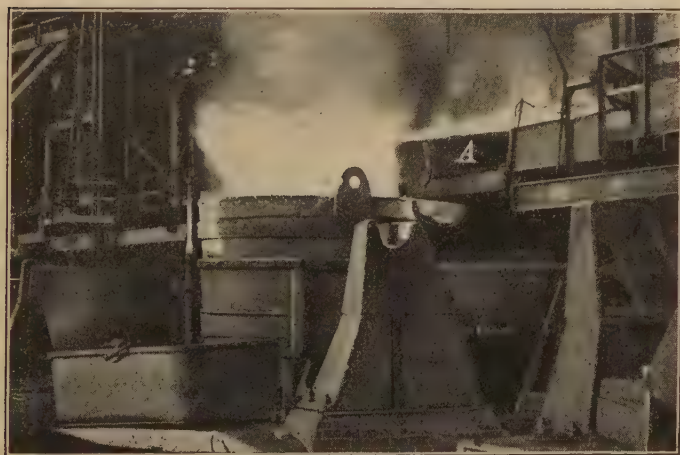


FIG. 233. Drawing off the molten steel from an open-hearth furnace into large buckets, from which it is cast into molds



FIG. 234. This figure illustrates how the properties of iron are modified by the presence of other substances. In the figure there are shown a number of iron objects about to be lowered into a bath of sulfuric acid. In order to clean the surface of the iron, since this element as well as its oxides are readily attacked by the acid. The important fact to note is that the bath containing the sulfuric acid is also made of iron, but along with the iron is a certain amount of silicon, these two elements forming an alloy which is only very slightly attacked by acids. This alloy is therefore used for making pipes and other objects which have to withstand the action of acids.

or cutting-tools. Steel assumes different color tints at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures as suited to the tempering of the tools specified

220°		paper cutters, wood-engraving tools
240°		knife blades, rock drills
260°		hand-plane cutters and cooper's tools
275°		axes, springs
290°		needles, screw drivers
300°		wood saws

Steel alloys. As we have seen (p. 373), small quantities of carbon greatly modify the properties of iron, and equally marked effects may be produced by a great many other elements. Accordingly, to secure a steel with the requisite properties, suitable percentages of these elements are added to the steel just before it is run out of the furnace. The elements most frequently added are manganese, silicon, nickel, chromium, tungsten, vanadium, and titanium, and steel containing an appreciable percentage of any of these elements is called a *steel alloy*. The element is added in the form of a rich alloy of iron, such as *ferrochromium* or *ferromanganese*.

The approximate composition and uses of some of the principal steel alloys are as follows:

3.5% nickel		armor plate
3.5% nickel and 3.5% chromium		armor plate and projectiles
12% manganese		burglar-proof safes
5.0% chromium and from 8 to 24% tungsten		high-speed lathe tools
6.0% chromium and 10% molybdenum		high-speed lathe tools
0.1% titanium		car rails and steel castings
0.1% vanadium		automobile parts
12 to 15% silicon		retorts for distilling acids

Compounds of iron. Iron differs from the metals so far studied in that it is able to form *two series* of compounds. In the one series the iron is *bivalent* and forms compounds which in formulas and many chemical properties are similar

to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *tervalent* metal and forms salts similar to those of aluminium. These salts are known as *ferric* compounds.

Ferrous salts. These salts are obtained by dissolving iron in the appropriate acid or, when insoluble, by precipitation. The crystallized salts are usually light-green in color.

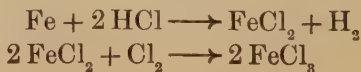
Ferrous sulfate (FeSO_4). Ferrous sulfate is the most familiar ferrous compound. It is usually obtained in the form of the hydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, called *copperas*, or *green vitriol*, and is prepared commercially as a by-product in the steel-plate mills. Preparatory to galvanizing or tinning (p. 348), steel plates are cleaned from rust by immersing them in dilute sulfuric acid, and in the process some of the iron dissolves. The liquors are concentrated, and the green vitriol separates from them. The salt is used in the manufacture of ink and iron alum and as a reagent to destroy weeds.

Ferrous sulfide (FeS). This occurs in nature as the yellowish-brown mineral *pyrrhotite*. In the laboratory it is made by heating iron and sulfur together for use in making hydrogen sulfide.

Iron disulfide (pyrite) (FeS_2). This compound occurs in nature in the form of brass-yellow cubical crystals often known as *fool's gold*. When pyrite is burned sulfur dioxide is produced; hence the mineral is used as a source of sulfur dioxide in making sulfuric acid.

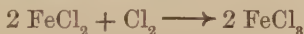
Ferric salts. The crystallized ferric salts are usually yellow or violet in color. Heated with water in the absence of free acid, they hydrolyze even more readily than the salts of aluminium. The most familiar ferric salt is the chloride.

Ferric chloride (FeCl_3). This salt can be obtained most conveniently by dissolving iron in hydrochloric acid and then passing chlorine into the solution:

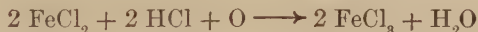


Ferric hydroxide ($\text{Fe}(\text{OH})_3$). When ammonium hydroxide is added to a solution of a ferric salt, there is formed a rusty-red precipitate which is generally regarded as ferric hydroxide ($\text{Fe}(\text{OH})_3$). Recent experiments, however, indicate that it is the oxide Fe_2O_3 , associated with a variable amount of water.

Oxidation of ferrous salts. When a ferrous salt in the presence of an acid is oxidized to a ferric salt, it will be noticed that the valence of the iron is increased from 2 to 3. This increase in valence can often be brought about without the aid of oxygen, as is shown in the following equation:

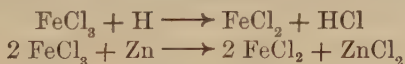


This is also called an oxidation, although no oxygen takes part in the reaction, for the same product is obtained as by the other method:



In general, when the valence of the metal of a salt is increased, the salt is said to be *oxidized*, whether any oxygen takes part in the reaction or not.

Reduction of ferric salts. Ferric salts may be changed into ferrous salts by the action of nascent hydrogen or other reducing agents, as shown in the following equations:

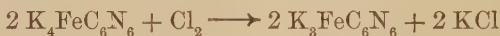


Although no oxygen is removed in either of these reactions, the ferric chloride is said to be *reduced*; and, in general, when the valence of the metal of a salt is diminished, the salt is said to be reduced.

Sodium ferrocyanide ($\text{Na}_4\text{FeC}_6\text{N}_6$); potassium ferrocyanide ($\text{K}_4\text{FeC}_6\text{N}_6$). These are the sodium and the potassium salts of the acid $\text{H}_4\text{FeC}_6\text{N}_6$ and are prepared from the by-products obtained in the manufacture of coal gas. They are both soluble yellow solids, and the potassium salt is often called *yellow prussiate of potash*. When a solution of either is added to a solution of a ferric salt such as ferric chloride, a deep-blue

precipitate of ferric ferrocyanide forms. This is called *Prussian blue*. It is used as a paint pigment and sometimes for bluing laundry water.

Potassium ferricyanide ($K_3FeC_6N_6$). By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are deposited which have the composition $K_3FeC_6N_6$:



This compound is called *potassium ferricyanide*, or *red prussiate of potash*.

Blue-printing. When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of *blue-printing*. A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, during which process the portions acted upon by the light turn blue, while the unaffected portions are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blue-print, since this base decolorizes the blue compound present.

COBALT AND NICKEL

Occurrence. Cobalt and nickel are almost always found together in ores which also contain iron, silver, and copper in combination with arsenic and sulfur. The richest deposits of cobalt are in Ontario, Canada. Nickel is also a frequent impurity of crude copper, and several million pounds of nickel sulfate are annually recovered in the United States in the refining of copper by electrolysis.

Properties and uses. Both these metals are silvery in appearance and take a high polish. They are somewhat heavier than iron and melt at a lower temperature. Their chief use is in making alloys. *Nickel steel is of the greatest importance* and is widely used for such purposes as the construction of parts of machinery, automobiles, locomotives, armor plate, and projectiles. An alloy of cobalt and chromium (*stellite*) is used



FIG. 235. The process of electroplating with nickel as carried out in a large factory

for making cutlery and lathe tools. *Nickel coinage* consists of copper and nickel, while German silver contains zinc in addition. Nickel is extensively used as a plating upon other metals (particularly upon brass) to prevent tarnishing in air, and cobalt can be used in the same way.

Electroplating with nickel. Nickel-plating is accomplished by an electrolytic process. The object to be plated is suspended in a solution of a nickel salt and serves as the cathode, while a plate of nickel is used as the anode. When the current is passing through the electrolyte the nickel is deposited in the form of a silverlike

coating upon the object to be plated, and an equivalent portion of nickel dissolves from the anode, the composition of the electrolyte remaining unchanged. Fig. 235 illustrates the process on a large scale, the objects to be plated being suspended from the rods *A, A*.

Cobalt oxide (CoO). This is the form in which most of the cobalt comes into the market. It is a black powder used in making other cobalt compounds and in making blue glass and blue decorations on china. Sometimes powdered cobalt glass, called *smalt*, is used instead of the oxide and as a pigment.

Salts of cobalt and nickel. Nearly all the simple salts of cobalt and of nickel have formulas similar to those of *ferrous* salts. The most familiar are the following:

$\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	a cherry-red deliquescent salt
$\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$	well-formed green crystals

INKS

Composition. Inks were known as early as 2500 B.C. and were used in writing. They were black and, like modern india ink, owed their color to carbon. The composition of ordinary black ink may be seen from the following formula, recommended by the United States government: tannic acid, 23.4 g.; gallic acid, 7.7 g.; ferrous sulfate, 30 g.; dilute hydrochloric acid, 25 g.; carbolic acid (phenol), 1 g.; suitable blue dye, 2.2 g.; sufficient water to make 1000 cc.

Tannic acid and the closely related compound gallic acid are obtained from the bark of various trees and especially from nutgalls (abnormal growths produced on parts of trees that have been stung by certain insects). *Ferrous salts* do not form a color with tannic and gallic acids, but *ferric salts* produce a black tannate and gallate of iron. When the ink is used the ferrous salt is oxidized by the air to a ferric salt, and this then forms the black iron compound. The dye called for in the formula is used to give a temporary color until the permanent color develops. The acid is necessary to keep the iron

in solution. The carbolic acid acts as a preservative to keep the ink from molding. *Circular No. 95*, issued by the United States Bureau of Standards, gives interesting information concerning inks.

Some special inks. The so-called *sympathetic inks* were used largely during the World War. When such inks are used the writing is invisible and remains so until the paper is heated or is treated with some substance that will unite with the compound composing the ink, to form a colored compound. A solution of lead acetate may be used for this purpose, the writing being developed by dipping the paper into a solution of hydrogen sulfide. A solution of cobalt chloride also serves the purpose, the writing being invisible until heated gently over a flame. If moistened with water, the writing again becomes invisible. *Indelible inks* are composed chiefly of silver nitrate dissolved in dilute aqua ammonia. When applied to paper (or fabric) the silver salt is slowly reduced to black metallic silver, which imparts the color and is not easily removed, since it is insoluble and inactive. For the same reason a solution of silver nitrate brought in contact with the skin slowly develops a black stain difficult to remove.

Removal of ink and other stains from textiles. Only some general principles can be stated. In the first place, the stain should be treated at the earliest moment. Thus, hot water will remove fruit stains and many ink stains if used while the stain is fresh. If active chemical substances are to be used, then a test should first be made upon a small clipping of the textile to see that no harm will result. *Especially is this important if the textile is colored*, since the substance used may act upon the dye. Fig. 236 shows a convenient way of applying chemicals to the stain.

To be successful one should know the nature of the stain and then determine the method of procedure. Some stains may be removed by physical methods alone. Thus, fruit stains and coffee

stains may usually be washed out with boiling water, while grease spots may be removed by placing the stain over some blotting paper and washing it with carbon tetrachloride or low-boiling gasoline. The grease is dissolved by the solvent, and the resulting solution is absorbed by the paper. If the grease is a solid, such as candle grease or paraffin, it may be removed from the fabric by placing the stained portion between blotting papers and pressing it with

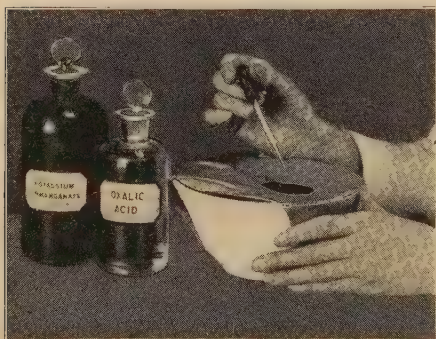


FIG. 236. Removing stains on textiles

a hot iron. The grease melts and is absorbed by the paper. Turpentine is a good solvent for paint spots, but must not be applied to silk. Many substances such as sir-ups may be washed out with water.

In many cases it is necessary to use chemical methods. Thus the red color produced by many acids may be removed by washing the stained portion of the fabric with a little dilute ammonia water. Nitric acid acts upon the cloth as well as upon the dye, so that the original color cannot be restored. Coffee and fruit stains, if not removed by boiling water, may be washed with a mild bleaching agent, preferably a solution of sodium hypochlorite, sold by the druggist under the name of *Javelle water*.

Ink stains, if not removed by boiling water, may be treated with lemon juice or with a dilute solution of oxalic acid. By this treatment the ferric salts in the ink are reduced to ferrous salts, which can then be washed out with water. Rust stains can be removed in a similar way. Some indelible-ink stains may be removed by soaking the fabric in a solution of sodium thiosulfate. *Silk is so sensitive to the action of solvents and reagents that it is generally impossible to remove stains from it without injuring the fabric.*

The whole subject of removal of stains from textiles is discussed in detail in *Farmers' Bulletin 861*, published by the United States Department of Agriculture.

EXERCISES

1. Suggest a reason why none of the metals so far studied occur free in nature.

2. The atomic weights of the members of the iron family are nearly identical. Are any of their properties correspondingly similar (see table at head of chapter)?

3. Which is the purest grade of iron?

4. What are the advantages and the disadvantages of cast iron?

5. Why is the basic open-hearth process used more than the Bessemer?

6. How would wrought iron or cast iron do for the construction of burglar-proof safes?

7. Why is it necessary to preheat the air blast used in the blast furnace but not in the Bessemer converter?

8. Give the common names of the ordinary hydrates of the sulfates of the following metals: sodium, magnesium, iron (ferrous).

9. How could you tell the difference between fool's gold and real gold?

10. Write the equation for the reaction which takes place when iron is dissolved in hydrochloric acid; in dilute sulfuric acid.

11. Contrast the relative advantages of iron and aluminium for making cooking utensils.

12. What would be a good test for a ferric salt?

13. Suggest a reason why some kinds of ink change color (blue to black) on drying.

14. What precautions must one take in removing stains with gasoline?

15. (a) Why are objects plated with nickel? (b) Is there any relation between nickel-plated objects and galvanized iron?

16. In what important reaction is nickel used as a catalytic agent?

17. Which contains the greatest percentage of iron: hematite, magnetite, or limonite?

18. What weight of iron would be required to make 100 kg. of copperas?

19. What weight of pyrite would be required to make 100 tons of 50 per cent sulfuric acid? (*Suggestion.* 1 gram-molecular weight of pyrite makes 2 gram-molecular weights of hydrogen sulfate.)

Refining of copper. If a pure copper is desired, then the blister copper must be refined. This is done by electrolysis. A large plate of it, serving as an anode, is suspended in a tank, facing a thin plate of pure copper which is the cathode. The tank is filled with a solution of copper sulfate and sulfuric acid to act as the electrolyte. An electric current passing through the cell dissolves copper from the anode and deposits it upon the cathode in pure form, while the impurities, including any gold and silver present, collect on the bottom of the tank. Electrolytic copper is one of the purest of commercial metals. Fig. 237 shows the pure copper cathode raised from an electrolytic cell so that it can be removed and the operation repeated.

Chemical conduct. Since copper is below hydrogen in the displacement series, hydrochloric acid and dilute sulfuric acid are almost without action upon it; hot concentrated sulfuric acid and nitric acid, however, readily dissolve it (pp. 170, 193). In moist air it slowly becomes covered with a film of the bright-red oxide Cu_2O , which soon changes to a green carbonate. Heated in the air the metal is easily oxidized to the black oxide CuO .

Uses. Copper is extensively used for electrical purposes, for roofs and cornices, for sheathing the bottoms of ships, and for making alloys. In the following table the composition of some of these alloys is indicated:

Aluminium bronze	90%-98% copper, 2%-10% aluminium
Brass	63%-73% copper, 27%-37% zinc
Bronze	70%-95% copper, 1%-25% zinc, 1%-18% tin
German silver	50%-60% copper, 20% zinc, 20%-30% nickel
Gold coin	10% copper, 90% gold
Silver coin	10% copper, 90% silver
Nickel coin	75% copper, 25% nickel

Electrotyping. Books are often printed from electrotype plates, which are prepared as follows: The face of the type is covered with wax, and this is firmly pressed down until a clear impression is obtained. The impressed side of the wax is coated with

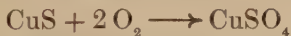
graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

Two series of copper compounds. Copper, like iron, forms *two series* of compounds: the *cuprous* compounds, in which it is univalent; and the *cupric* compounds, in which it is bivalent. The only important cuprous compound is the oxide Cu_2O , which is a bright-red solid sometimes used to impart a ruby color to glass.

Cupric compounds. Cupric salts are easily made by dissolving cupric oxide in acids or, when insoluble, by precipitation. In crystallized form most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are frequently called merely copper salts.

Cupric oxide (CuO). This is a black solid obtained by heating copper in excess of air or by igniting the hydroxide or the nitrate. It is used as an oxidizing agent.

Cupric sulfate (CuSO_4). When crystallized from water, copper sulfate forms large blue crystals of the hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, called *blue vitriol* or *bluestone*. The salt is a by-product in silver refining and is also made by the oxidation of pyrite containing copper sulfide:



Blue vitriol is used in electrotyping, in copper refining, and in the manufacture of insecticides. Like all copper salts it is poisonous, especially to lower forms of life. When added, even in minute quantities, to water containing green pond scum (algæ) the plant is quickly killed. The mixture obtained by treating blue vitriol with a solution of calcium hydroxide (which precipitates copper hydroxide) is called *Bordeaux mixture* and is used as a spray for killing molds and scale on fruit trees.

Cupric sulfide (CuS). In the form of a black insoluble precipitate cupric sulfide (CuS) is easily prepared by the action of hydrogen sulfide upon a solution of a copper salt:



MERCURY

Properties and occurrence. Mercury stands out prominently among the metals for being the only one that is *liquid at ordinary temperatures*. Its use in thermometers and barometers, under the common name of *quicksilver*, has made it familiar to everyone. It has long been known and was a favorite with the alchemists. Its most common ore is the sulfide HgS, known as *cinnabar*. This occurs in quantities in Spain and was mined even as early as Roman times for use as a red pigment. The same sulfide, made in the laboratory by heating mercury and sulfur together, still constitutes a valuable pigment known as *vermilion*. Although a liquid, mercury is much heavier than iron (density 13.56). It boils at 357° and freezes at -38.87°.

Metallurgy. Mercury is easily separated from cinnabar. It is only necessary to roast the ore in air, when the sulfur burns, leaving the mercury. Spain leads in the production of the metal, followed by California.

Chemical conduct. When mercury is heated *at a low temperature* in the air, it slowly unites with oxygen to form mercuric oxide HgO; at higher temperatures this decomposes into its elements (p. 16). Toward acids mercury conducts itself very much like copper.

Uses. In addition to its use in thermometers and barometers, mercury is used as a liquid over which to collect gases that are soluble in water. It readily combines with metals to form alloys called *amalgams*, and this property is turned to account in extracting gold and silver from their ores.

The common material sold for filling teeth is an amalgam of silver and tin.

Compounds of mercury. Like copper, mercury forms two series of compounds: the *mercurous* compounds, such as mercurous chloride (HgCl); and the *mercuric* compounds, represented by mercuric chloride (HgCl_2).

Mercuric oxide (HgO). Mercuric oxide is usually obtained as a brick-red substance by carefully heating the nitrate:



It can also be obtained in a yellow form.

Mercurous chloride (calomel) (HgCl). Being insoluble, mercurous chloride is precipitated as a white solid when a soluble chloride is added to a solution of mercurous nitrate:



It is a much-used medicine.

Mercuric chloride (corrosive sublimate) (HgCl_2). This substance is made on a commercial scale by heating a mixture of common salt and mercuric sulfate:



The mercuric chloride, being readily volatile, vaporizes and is condensed again in cool vessels. It resembles mercurous chloride in being a white solid, but it is soluble in water. *It is extremely poisonous*, and in dilute solutions is used as an antiseptic in dressing wounds.

Mercuric sulfide (HgS). As *cinnabar*, this substance forms the chief native compound of mercury and occurs in red crystalline masses. By passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is precipitated as a *black* powder insoluble in water and acids. By other means it can be prepared as a brilliant red powder, known as *vermilion*, which is used as a pigment in fine paints.

SILVER

Properties and occurrence. Silver has been known from the earliest times and, together with gold, has always ranked as a precious metal. The Romans called it *argentum* and used it for ornamental purposes and for coins. Like copper, it occurs native as well as in the form of compounds. Most often it occurs in combination with sulfur (Ag_2S) or as a constituent of other sulfides. In the United States it is for the most part produced in connection with lead. The United States produces over one third of the world's output of silver, and the American continent about 80 per cent.

Silver is a heavy, rather soft white metal, very ductile and malleable. It is the best conductor of heat and electricity. It melts a little lower than copper and, like gold, alloys easily with other metals. In the form of a fine powder it is black.

Chemical conduct and uses. Silver is not acted upon by either water or air. Sulfur and its compounds tarnish it, forming black silver sulfide (Ag_2S). Nitric acid is its best solvent,

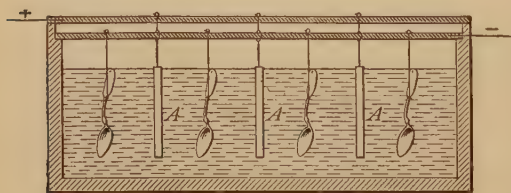


FIG. 238. The process of silver plating

forming silver nitrate (AgNO_3). When its compounds are reduced in a glass vessel the pure metal is deposited as a shining

film on the sides of the vessel; hence its use in making *mirrors*. Its use for making tableware, ornaments, and coins is well known. Silver coins contain 90 per cent of silver and 10 per cent of copper.

Electroplating with silver. Since silver is not acted upon by water or air and has a pleasing appearance, it is used to coat various articles made of cheaper metals. Such articles are said to

be *silver plated*, and the process by which this is done is very similar to electroplating with nickel (Fig. 235). The object to be plated (as, for example, a spoon) is attached to a wire and dipped into a solution of a suitable silver salt. Electrical connection is made in such a way that the article to be plated is the cathode (Fig. 238), while the anode *A* is made up of one or more plates of silver.

Compounds of silver. Silver forms only one series of salts, which corresponds to the mercurous and the cuprous series.

Silver nitrate (lunar caustic) (AgNO_3). This salt is a white solid and is easily prepared by dissolving silver in nitric acid and evaporating the resulting solution. When cast into sticks it is called *lunar caustic*, for it has a very corrosive action on flesh and is sometimes used in surgery to burn away abnormal growths.

The alchemists designated the metals by the names of the heavenly bodies. The moon (*luna*) was the symbol for silver; hence the name *lunar caustic*.

Compounds of silver with the halogens. The chloride, the bromide, and the iodide of silver (often termed collectively the *silver halides*) are insoluble in water and in acids and therefore are precipitated by bringing together a soluble halogen salt with silver nitrate:



They are remarkable for the fact that they are very sensitive to the action of light, undergoing a change of color and chemical composition when exposed to sunlight, especially if in contact with organic matter, such as gelatin. It is upon this property of the silver halides that the art of photography is based.

Photography. From a chemical standpoint the processes of photography may be described under two heads: (1) the preparation of the negative; (2) the preparation of the print.

1. Preparation of the negative. The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is

sometimes added also), over a glass plate or more often a nitro-cellulose film (Fig. 150) and allowing it to dry. When the plate so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a change (not well understood) which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is therefore called *latent*. It can be made visible by the process of *developing*.

To develop the image the exposed plate is immersed in a solution of some reducing agent called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is deposited in the form of a black film which adheres closely to the plate.

The unaffected silver salt is now removed from the plate by immersing it in a solution of sodium thiosulfate (*hypo*) (p. 310). The plate is then washed with water and dried. The plate so prepared is called the *negative* (Fig. 241) because it is a picture of the object photographed, with the lights and positions exactly reversed.

2. Preparation of the print. The print is made on paper which is prepared in much the same way as the negative plate. The negative is placed upon this paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride a visible image is produced, in which case a developer is not needed. *Proofs* are made in this way. In order to make them permanent the unchanged silver chloride must be dissolved off with sodium thiosulfate. The print is then *toned* by dipping it into a solution of gold or platinum salts, in which process the silver on the print passes into solution, while the gold or platinum takes its place. These metals give a characteristic color or tone to the print, the gold making it reddish brown, while the platinum gives it a steel-gray tone. Since the darkest places on the negative cut off the most light, it is evident that the lights of the print (Fig. 242) will be the reverse of those of the negative and will therefore correspond to those of the object photographed.



FIG. 239. Dissolving silver in nitric acid preparatory to making the silver halides used in photographic films

One company uses 6000 pounds of silver weekly for this purpose



FIG. 240. Nitrating cotton for the manufacture of photographic films

The cotton is led down through the inclined tubes into the kettles, which contain a mixture of nitric and sulfuric acids



FIG. 241. The negative plate

The photographic plate or film, after exposure in the camera, is immersed in a solution of a reducing agent (the developer) which reduces the silver salt that has been acted upon by the light to black metallic silver. The unaffected silver salt is then dissolved, leaving a picture of the object photographed on the plate, but with the lights and positions exactly reversed.

The plate so prepared is called the *negative*



FIG. 242. The positive print

The print is made from the negative. The photographic paper on which the print is to be made is placed under the negative and exposed to the light. The paper is then treated with a developer, and the unaffected silver salts are dissolved off as in the preparation of the negative. Since the darkest places on the negative cut off the most light, the lights of the print will be the reverse of those of the negative; in other words, they will correspond to those of the object photographed

EXERCISES

1. Point out some respects in which copper and mercury resemble each other.

2. Note the position of copper, mercury, and silver in the displacement series. What facts concerning these metals could you predict from their position in the series?

3. (*a*) Which of the metals studied are found in a free state in nature? (*b*) What is their position in the displacement series with reference to hydrogen?

4. (*a*) Which of the metals so far studied is the heaviest? the lightest? (*b*) Which has the highest melting point? the lowest melting point? (Consult table in Appendix.)

5. What metal other than copper is used in making wires for conducting electricity?

6. Give the composition of a nickel coin; a silver coin; a gold coin.

7. What is the distinction in composition between brass, bronze, and German silver?

8. What is the distinction in composition between blue vitriol and copperas?

9. What are the properties of mercury that make it well adapted for use in thermometers and barometers?

10. What are the extremes of temperature that can be registered by an ordinary thermometer?

11. Some thermometers have the space above the mercury filled with nitrogen. Can you suggest any reason for this?

12. Give the composition of each of the following: calomel, corrosive sublimate, lunar caustic, vermilion.

13. Suppose you got mercury in contact with a gold ring. What would be the result?

14. A solution of copper sulfate reacts acid to litmus. Explain.

15. What will happen if you put your knife blade into a solution of copper sulphate?

16. The alchemists claimed that by putting iron into copper sulfate solution the iron was changed into copper. Point out the fallacy.

17. Why do silver spoons blacken when they come in contact with certain foods?

18. The shutter on a camera did not open, so that the film was not exposed. Not knowing this the photographer proceeded with the film as usual. What results would he obtain?

19. A photographic film was accidentally exposed to the light before it was placed in the camera. What results would be obtained when the plate was developed and treated in the usual way?

20. What are the steps in making silver bromide from the metallic silver?

21. What is the disadvantage in using nitrocellulose for making photographic films?

22. Suppose you wish to electroplate a metal tablet with copper, how would you proceed?

23. How could you easily distinguish between mercuric oxide and cupric oxide?

24. (a) Explain the chemistry involved in toning a print (p. 161).
(b) Could a print be toned by placing it in a solution of copper salt?

25. Suppose you were given the following substances: sulfuric acid, hydrochloric acid, nitric acid, marble, copper, and zinc. What gases could you prepare from these substances?

26. Suppose you wish to prepare calomel and corrosive sublimate on a large scale, what raw materials would you require?

27. Suppose you were using chalcopyrite as a source of copper and wished to obtain 100 tons of the metal, what weight of the ore would be required?

28. What is the percentage of mercury in cinnabar?

29. A silver dollar weighs approximately 26.5 g. What weight of silver nitrate could be made from such a coin?

30. It has been stated that a single photographic plant uses 6000 lb. of silver weekly for photography. What weight of silver bromide would this quantity of silver make?

CHAPTER XLIII

TIN AND LEAD

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	COMMON OXIDES		
Tin	Sn	118.70	7.30	231.9°	SnO	SnO ₂	
Lead	Pb	207.20	11.37	327.4°	PbO	Pb ₃ O ₄	PbO ₂

TIN

Occurrence. Tin has long been used and is familiar to all of us. The ancients confused it with lead, but about the beginning of the Christian era the distinction between the two came to be recognized. The element occurs in nature chiefly in the form of the oxide SnO₂, which is known as *cassiterite* or *tin stone*. This is found principally in Malaya, Bolivia, Banka, and China and is the ore from which our supply of the metal comes. Practically none is produced in the United States.

Properties. Pure tin, called *block tin*, is a soft white metal with a silverlike appearance and luster; it melts readily and is somewhat lighter than copper. It is malleable and can be rolled out into very thin sheets, forming *tin foil*; most tin foil, however, contains a considerable percentage of lead.

Metallurgy. The metallurgy of tin is very simple. It is only necessary to heat the ore with carbon, which removes the oxygen:



Chemical conduct. Under ordinary conditions tin is unchanged by air or moisture, but at a high temperature it burns,

forming the oxide SnO_2 . Dilute acids have little effect upon it, but concentrated acids attack it readily. Concentrated hydrochloric acid changes it into the chloride SnCl_2 .

Uses of tin. A great deal of tin is used in the making of *tin plate*. The process consists in dipping thin sheets of iron into the melted tin and is quite similar to that of galvanizing iron (p. 348). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, such as in roofing and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin. *Pewter* and *soft solder* are alloys of tin and lead.

Soldering and brazing. The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder, and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable flux must be used which will either *dissolve* the oxide as fast as it forms or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing* or *hard soldering* the process is essentially the same except that a low-melting brass is used instead of solder, and borax is used as a flux (p. 291).

Compounds of tin. Tin forms two series of metallic compounds: the *stannous*, in which the tin is bivalent, as is illustrated in the compounds SnO , SnS , SnCl_2 ; and the *stannic*, in which it is quadrivalent, as shown in the compounds SnO_2 , SnS_2 .

Chlorides of tin. *Stannous* chloride is prepared by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. If metallic tin is heated in a current of dry chlorine, *anhydrous* stannic chloride (SnCl_4) is obtained as a heavy, colorless liquid which fumes strongly on exposure to air. A great deal of tin in the form of stannic

chloride is recovered from scrap tin by the action of chlorine. From solution in water a solid hydrate is obtained of the formula $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$.

The chlorides of tin are much used as mordants in dyeing processes, in calico printing, and to give weight to silk.

In the World War hand grenades containing an explosive charge and stannic chloride were used to clear dugouts of enemy troops. The explosion of the grenades filled the dugouts with a fine mist of the chloride so that one could not breathe the air without painful suffocation.

LEAD

Properties. Articles made of lead have been found in very old Egyptian ruins, and there is no doubt but that it was used from early times. The Romans called it *plumbum* and used it for water pipes, as we do today. It is a heavy metal which has a bright luster on a freshly cut surface but soon tarnishes on exposure to air. It is soft, easily melted, and has little strength.

Occurrence. The United States produces about one third of the world's supply of lead, the chief lead-producing states being Missouri, Idaho, Utah, and Colorado. The chief ore is *galenite* (PbS) (Fig. 243), and it usually contains some silver.

The metal is separated by a rather complicated process of roasting and reduction, and the crude lead is alloyed with any silver present in the ore and also with smaller percentages of other metals with which galena is associated. It is partially purified by melting it in a furnace with free access of air. Some of the impurities are thus changed into oxides, which float on the surface of the molten lead and so can be removed. The silver, however, still remains alloyed with the lead, from which it is separated by suitable processes.

Chemical conduct. When lead is heated in the air it forms a yellow oxide (PbO). With the exception of hydrochloric and sulfuric acids (which form insoluble compounds), most acids,

even very weak ones, act upon the metal, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it to a slight extent.

Uses. Lead finds many important applications in the industries, chiefly in the manufacture of storage batteries, in linings for sulfuric acid plants, in alloys of various kinds (such as shot, antifriction metals, type metal, and pewter),



FIG. 243. A crystal of galenite embedded in calcite

and in water pipes for plumbing. Since lead dissolves to some extent in pure water, it should not be used for pipes that are to carry rain water. *About one third of the annual production of lead is used in making paint and is permanently lost.*

Compounds of lead. In nearly all its compounds lead is bivalent, but in a few of its compounds it has a valence of four. All its compounds are poisonous to some extent.

Lead oxides. Lead forms a number of oxides, the most important of which are the following:

1. **Litharge (PbO).** This oxide forms when lead is oxidized at a little less than 1000° and is obtained as a by-product

in silver refining. In color it ranges from yellow and light brown to red, depending on its mode of production. It has a number of commercial uses.

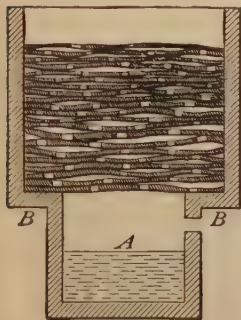


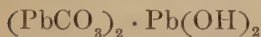
FIG. 244. A crock filled with thin lead plates for making white lead

2. *Red lead, or minium* (Pb_3O_4). Minium is prepared by heating lead (or litharge) to about 450 degrees in contact with a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron.

Lead sulfide (PbS). In nature this compound occurs in a highly crystalline form called *galenite* (Fig. 243), the crystals having much the same color and luster as pure lead. It is readily prepared in the laboratory as a black precipitate, by the action of hydrogen sulfide upon soluble lead salts:



Lead carbonate. The normal carbonate of lead ($PbCO_3$) is found to some extent in nature and can be prepared in the laboratory; a basic carbonate, however, can be obtained much more easily. This is a compound of lead carbonate and lead hydroxide. It has the formula



and is commonly called *white lead*. It is prepared

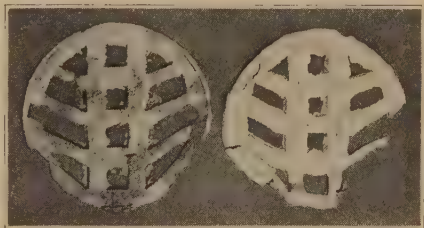


FIG. 245. Lead buckles before and after exposure to acetic acid and carbon dioxide

on a very large scale as a white pigment and as a body for paints which are to be colored with other substances.

Manufacture of white lead. White lead can be prepared by a number of processes, but no other seems to produce a product of as desirable physical properties as the old Dutch process, which has been used for centuries, though with many improvements. In this process the lead is cast into perforated plates called *buckles*, which are placed loosely upon each other in a crock of the shape



FIG. 246. Harvesting flax

Its seeds when pressed give us linseed oil, while the residue is a valuable cattle food. Linen is made from the stems of the plant

shown in Fig. 244, the ledge *B* formed by the constriction of the crock supporting the plates. Under them, in *A*, is poured a suitable quantity of dilute acetic acid, and the crocks so charged are placed in banks and covered with stable manure or spent tanbark. The heat of fermentation in the latter warms the acid, the fumes of which attack the lead, forming lead acetate. The carbon dioxide from the fermentation enters into reaction with the acetate and produces the basic carbonate, regenerating acetic acid, which acts again upon the lead. The process continues until the buckles are almost completely converted into the desired compound. Fig. 245 shows a buckle before and after corrosion.

OTHER IMPORTANT COMPOUNDS OF LEAD

Lead nitrate ($\text{Pb}(\text{NO}_3)_2$): white soluble crystals

Lead chloride (PbCl_2): white needles, very sparingly soluble

Lead sulfate (PbSO_4): an insoluble white crystalline powder

Lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$): a soluble white salt called *sugar of lead*

Lead chromate (PbCrO_4): used as a pigment in paint (*chrome yellow*)

PAINTS

Composition. A paint consists of three essential ingredients: the *vehicle*, the *body*, and the *pigment*.

1. **The vehicle, or liquid medium.** This must be an oil *which will dry rapidly and harden in drying to a more or less flexible, hornlike body*. These changes in the oil are due to oxidation by the air. A number of different oils will serve this purpose, but linseed oil (Fig. 246) has long been used as the standard drying oil, since it can be produced in quantity and at moderate cost. It is customary to add to it a *dryer*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation.

2. **The body.** The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries and will have good covering power. While white lead meets these requirements, it is moderately expensive, and it also blackens

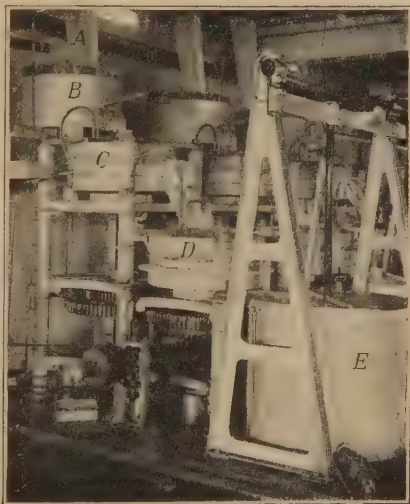


FIG. 247. Factory appliances used in mixing and grinding paint



FIG. 248. Making incisions in pine trees

From these incisions exudes a resinous mass which is the raw material from which ordinary rosin and oil of turpentine are prepared

cases they are natural products. Sometimes they are prepared by precipitating an amorphous body (usually a colloid) in the presence of an organic dye, the dye being adsorbed by the precipitate and giving it a color. Such pigments can be prepared in endless variety of colors and are called *lakes*. They are usually not so permanent as mineral pigments but serve the purpose very well.

when exposed to hydrogen sulfide, which is likely to be present in the air in cities. Other bodies are now frequently combined with the lead or replace it altogether, among them being zinc oxide, barium sulfate, and a product called lithopone (p. 349). For some purposes these materials are a real advantage, and they are not to be regarded as adulterants unless sold as white lead.

3. The pigment, or coloring matter. In the case of white paints the body serves also as the coloring matter. For other colors a specific pigment must be added. Frequently these pigments are metallic oxides or salts and in most



FIG. 249. The resinous mass (1) which exudes from pine trees (Fig. 248), when distilled, yields oil of turpentine (3), sometimes known as *spirits of turpentine*, and leaves a residue (2) which is ordinary rosin, used in making cheap soaps and for many other purposes

Fig. 247 represents the method of manufacture of paint. The body, together with a little oil, enters at *A* and is ground in succession in *B*, *C*, *D*, and *E*, during which process the requisite amounts of oil, dryer, and pigment are added.

Varnish. Varnish is a liquid which, on being applied to a surface and left to stand, forms a closely adhering and generally



FIG. 250. Making varnish

The resin is placed in large iron kettles set on wheels, and melted over a fire. The kettles are then drawn away from the fire, and the resin is dissolved in linseed oil together with oil of turpentine or a similar liquid, such as benzine

transparent film. Varnishes are made by dissolving in appropriate solvents the resins (or gums) obtained from certain trees. There are two chief kinds: (1) In the one the resin is dissolved in linseed oil (Fig. 250) *thinned* with spirits of turpentine or a similar liquid, such as benzine. On exposure to the air the turpentine evaporates and the linseed oil oxidizes and dries as in paints. (2) In the other class, known as *spirit varnishes*, the resin is dissolved in some volatile liquid, as spirits of turpentine or alcohol. On exposure to air the solvent quickly evaporates, leaving the resin.

Spirits of turpentine and rosin (which is not a true resin, but is sometimes used in varnish) are obtained from pine trees, especially from a species that grows in the Southern states (Figs. 248, 249).

EXERCISES

1. How could you distinguish between tin and lead?
2. (a) What commercial products consist of some one metal coated with a layer of a second metal? (b) What is the object of using the two metals in each case?
3. What salts other than those of tin are used as mordants?
4. Which of the compounds of tin is a liquid?
5. How could you distinguish between lead oxide (PbO) and mercuric oxide (HgO)?
6. How can you remove paint from clothing?
7. Mention different substances studied that are obtained from trees of various kinds.
8. Which of the lead compounds studied have a color?
9. Which of the metals studied are not produced to any extent in the United States?
10. What properties have spirits of turpentine, alcohol, and benzine in common that adapt them for use in making varnish?
11. Are there any objections to using benzene as a solvent in making varnish?
12. Linseed oil is more expensive than cottonseed oil. Why not use the latter in making paint?
13. Painters using white lead often suffer from lead poisoning. Magnesium sulfate is said to be a good antidote for lead poisoning. Explain its action. (*Suggestion.* A compound must be soluble in order to be absorbed in the system.)
14. Mention an alloy of tin; of lead.
15. For what purposes is rosin used in addition to making varnish?
16. What weight of tin will one ton of cassiterite give on reduction?
17. Suppose you wish to prepare 100 kg. of stannic chloride for use in silk manufacture, what weight of tin will be required?
18. What is the per cent of lead in galenite?

CHAPTER XLIV

MANGANESE AND CHROMIUM

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF ACIDS
Manganese	Mn	54.93	8.01	1230°	H ₂ MnO ₄ and HMnO ₄
Chromium	Cr	52.00	7.30	1615°	H ₂ CrO ₄ and H ₂ Cr ₂ O ₇

General. Manganese and chromium, although in different periodic families, may be discussed together. The metals themselves are important constituents of some of the steel alloys.

MANGANESE

Occurrence and properties. It will be recalled that in the preparation of both oxygen and chlorine the oxide MnO₂ was used. This compound occurs in nature as the mineral *pyrolusite* and is the ore from which manganese and its compounds are prepared. The largest deposits are in Brazil and India, but during the World War, when it was difficult to secure adequate supplies from these countries, considerable manganese ore was mined in the United States.

The metal is hard and brittle and looks somewhat like iron. Its density and melting point are not far from those of iron. It liberates hydrogen from dilute acids and from water.

Metallurgy. The pure metal is best prepared by the Goldschmidt process (p. 356). By reducing a mixture of oxides of iron and manganese there are obtained alloys of the two metals, known as *spiegel iron* and *ferromanganese*.

Compounds of manganese. Manganese not only forms salts like the other metals but also forms unstable acids, some of whose salts are of great importance.

Manganese salts. Manganese resembles iron in that it acts both as a bivalent and a trivalent metal. The *manganous salts*, in which the metal is bivalent, are the only important ones. These have formulas similar to the ferrous salts and resemble them in many of their chemical properties. Most of them are pink in color.

Permanganic acid (HMnO_4); potassium permanganate (KMnO_4). Potassium permanganate is a salt of the unstable *permanganic acid* (HMnO_4). It forms deep-purple crystals readily soluble in water. It is a powerful oxidizing agent and is used for this purpose both in the laboratory and as a disinfectant and an antiseptic.

Oxidizing properties of potassium permanganate. Potassium permanganate is remarkable for its strong oxidizing properties, especially in the presence of an acid. When sulfuric acid is present the reaction takes place in such a way that *both the potassium and the manganese are changed into sulfates*, with the liberation of oxygen, as shown in the equation



Under ordinary conditions, however, the reaction does not take place unless a third substance is present which is capable of oxidation. The oxygen is not given off in the free state, but is used up in effecting oxidation.

CHROMIUM

General. Chromium is a hard metal about as heavy as iron. The only important ore is *chromite* or *chrome iron ore*, which has the composition FeCr_2O_4 . This ore is found chiefly in Rhodesia, New Caledonia, and Greece. A small amount occurs in California. The metallurgy of the metal is similar to that of manganese.

Compounds of chromium. Like manganese, chromium acts both as a base-forming and an acid-forming element. Nearly all its compounds are colored; hence the name *chromium*, which is derived from a word meaning "color."

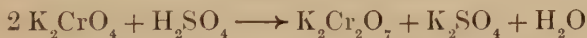
Chromic hydroxide ($\text{Cr}(\text{OH})_3$); chromic salts. Chromic hydroxide is a greenish compound. It is insoluble and can therefore be prepared by precipitation. It dissolves in acids, forming the corresponding *chromic salts*. These are green or violet in color and have formulas similar to the ferric salts. They are used as mordants (p. 363).

Chromates. The chromates are salts of the unstable *chromic acid* (H_2CrO_4) and as a rule are yellow in color. Most of the chromates are insoluble and can be prepared from the soluble potassium salt by precipitation. In the case of lead chromate the equation is as follows:



Lead chromate (*chrome yellow*) and barium chromate are used as yellow pigments.

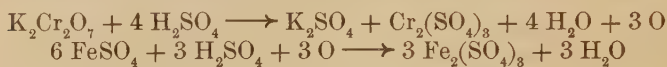
Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). When potassium chromate is treated with sulfuric acid, the potassium salt of *dichromic acid* ($\text{H}_2\text{Cr}_2\text{O}_7$) is formed:



This is the best-known dichromate and the most familiar chromium compound. It forms large brilliant crystals of a red color and is rather sparingly soluble in water. Potassium dichromate, as well as the corresponding sodium salt ($\text{Na}_2\text{Cr}_2\text{O}_7$), finds use in many industries as an oxidizing agent, especially in the preparation of organic substances and in the construction of several kinds of electrical batteries.

Oxidizing action of potassium dichromate. When a dilute solution of potassium dichromate or sodium dichromate is treated with sulfuric acid, no reaction apparently takes place. However, if

there is present a third substance capable of oxidation, the dichromate gives up a portion of its oxygen to this substance, and both the potassium and the chromium are converted into sulfates. The oxidation of ferrous sulfate by potassium dichromate is a good illustration, the reaction being represented in two steps:



This reaction is often employed in the analysis of iron ores.

EXERCISES

1. For what purposes are steel alloys containing manganese and chromium used?
2. What four uses of manganese dioxide (pyrolusite) have been mentioned?
3. Manganese dioxide in powdered form resembles charcoal powder. How could you easily distinguish between the two?
4. Instances are on record where charcoal was mistaken for manganese dioxide and used with the intention of preparing oxygen, with the result that a very serious explosion took place. Explain.
5. (a) Write the equations for the reactions which take place when manganese (bivalent) dissolves in hydrochloric acid; in dilute sulfuric acid. (b) What are the names of the resulting salts?
6. What is the Goldschmidt process?
7. When manganese dioxide is used in preparing chlorine what compound of manganese is formed?
8. How could you prepare manganous sulfide (insoluble) from manganous chloride (soluble)?
9. (a) What important sulfates have we studied that are colorless? (b) What ones are colored?
10. When a solution of potassium permanganate is used as an oxidizing agent, the deep-purple color of the solution changes to a pale pink. Explain (see equation, p. 412).
11. (a) What substances studied are used as disinfectants? (b) What are used as antiseptics?
12. What metal studied, in addition to manganese and chromium, forms acids?

13. (a) Write the equation for the reaction which takes place when chromic hydroxide is neutralized by sulfuric acid. (b) What is the name of the resulting salt?

14. The common cleaning fluid used in the laboratory for cleaning test tubes and beakers consists of a mixture of sodium dichromate and sulfuric acid. Wherein does its efficiency lie?

15. What weight of potassium permanganate could be prepared from 100 kg. of pyrolusite, assuming that all the manganese of the ore is utilized? (*Suggestion.* 1 gram-molecular weight of the ore will form 1 gram-molecular weight of the permanganate.)

16. 200 lb. of ferrochromium containing 40 per cent of chromium was added to a ton of steel. What per cent of chromium did the resulting alloy contain?

CHAPTER XLV

PLATINUM AND GOLD

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Platinum	Pt	195.2	21.50	1755°
Gold	Au	197.2	19.32	1063°

General. Gold has been known from the earliest times and has always been highly prized. The Romans called it *aurum*, from which word its symbol is derived. We commonly think of gold as the most valuable of the precious metals, yet platinum is worth about five times as much. The value of gold and platinum depends partly upon their relative scarcity, partly upon their properties, and partly because the money value of gold is fixed by law. Neither of them is acted upon by air or water. They are inactive toward most reagents and will not dissolve in the common acids, although readily soluble in *aqua regia*. Both are very heavy, and the melting point of platinum is high.

GOLD

Properties. Gold is a very heavy bright-yellow metal, exceedingly malleable and ductile, and a good conductor of electricity. Its melting point (1063°) is much below that of platinum. It is quite soft and is usually alloyed with copper or silver to give it the hardness required for most practical uses. The degree of fineness is expressed in terms of *carats*, pure gold being 24 carats; the gold used for jewelry is usually 18 carats, 18 parts being gold and 6 parts copper or silver.

Gold coinage is 90 per cent gold and 10 per cent copper. Gold is the basis of international credit, and its price is fixed at \$20.67 per troy ounce.

Occurrence. South Africa produces the most gold. The United States produces about one fifth of the world's supply, Alaska, California, Colorado, and Nevada leading in its



FIG. 251. Breaking down gold-bearing deposits by streams of water

production. Traces of it are found in almost all soils and even in sea water, but the cost of its production from such sources far exceeds the value of the metal extracted.

Extraction. The extraction of gold is accomplished in a number of ways, according to the character of the deposit. In placer mining the gold-bearing sand is washed by a current of water which is so regulated that particles of light weight are swept away, while the heavier gold is obtained as a sediment. In hydraulic mining the earth and sand are swept into sluices by powerful streams of water operated by pumps. In quartz mining the quartz is stamped to powder and is then washed over copper

plates, the surfaces of which have been amalgamated. The particles of gold stick to the mercury or dissolve in it, the gold being recovered by distillation. In other cases, especially when the gold is in very fine powder or in chemical combination, chemical reactions are employed. In the cyanide process the gold-bearing material is treated with a dilute solution of sodium cyanide, with free access of air. The gold dissolves to form a complex cyanide, from which it can be precipitated by metallic zinc or by electrolysis.

In the chlorination process the ore is treated with chlorine, which converts the gold into the soluble trichloride AuCl_3 . It is recovered from this solution by suitable precipitants.

Chemical conduct. Gold is not attacked by any one of the common acids; aqua regia easily dissolves it, forming *chlorauric acid* (HAuCl_4). Fused alkalies also attack it. Most oxidizing agents are without action upon it, and in general it is not an active element.

PLATINUM

Properties. Platinum is a grayish-white metal of high luster and is very malleable and ductile. It has a relatively high melting point (1755°) and is a good conductor of electricity. In finely divided form it has the ability to adsorb gases, especially oxygen and hydrogen. These adsorbed gases are in a very active condition, resembling the nascent state, and can combine with each other at ordinary temperatures. A jet of hydrogen or coal gas directed upon spongy platinum quickly ignites.

Occurrence and production. In normal times Russia furnishes by far the largest quantity of platinum. Thus in 1914 (previous to the World War) that country produced 241,200 troy ounces out of a total world's production of 263,453 ounces. During the war the supply was cut off, while the demand for the metal for use as a catalyzer in the production of certain chemicals greatly increased. As a result, the price rose from about \$45 to over \$100 per troy ounce.

Chemical conduct. Platinum is a very inactive element chemically and is not attacked by any of the common acids. Aqua regia slowly dissolves it, and it is also attacked by fused alkalis. It combines at higher temperatures with carbon and phosphorus and forms alloys with many metals. It is readily attacked by chlorine but not by oxidizing agents.

Platinum as a catalytic agent. Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid. When desired



FIG. 252. Some laboratory utensils made of platinum

for this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos*. The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent. Some other metals possess this same power, notably *palladium*, which is remarkable for its ability to adsorb hydrogen.

Applications. Platinum is very valuable as a material for the manufacture of chemical utensils which are required to stand a high temperature or the action of strong reagents. Platinum crucibles, dishes, forceps, electrodes, and similar articles (Fig. 252) are indispensable in the chemical laboratory. A considerable percentage of the supply of the metal is used

in dentistry. In the industries platinum is used as a catalytic material in a number of reactions. A large fraction of the annual production is used for jewelry. Its use in jewelry is due primarily to its high cost. It is unfortunate that it should be so used, because of the limited supply and its importance in necessary industries.

Chloroplatinic acid (H_2PtCl_6). When platinum is dissolved in aqua regia and the solution is evaporated to dryness, orange-colored crystals of *chloroplatinic acid* (H_2PtCl_6) are obtained. The potassium and ammonium salts of this acid are nearly insoluble in water and alcohol.

EXERCISES

1. In what respects do gold and platinum differ from the other metals studied?

2. Compare the densities of platinum and silver; of gold and copper.

3. What is fool's gold?

4. Platinum and silver resemble each other in appearance. How could you easily distinguish between them?

5. What are the relative costs of gold and platinum?

6. What is the position, in the displacement series, of the metals that occur free in nature?

7. (a) What action would take place if a strip of metallic silver were placed in solution of gold and platinum compounds? (b) In what process is advantage taken of this action?

8. Mention three substances used for imparting a ruby color to glass.

9. (a) What are the properties which make platinum so valuable for use in the manufacture of chemical utensils? (b) Why not use gold in its place?

10. What action would take place if nitric acid were added (a) to gold? (b) to a gold coin?

11. A five-dollar gold piece weighs approximately 8.334 g. What weight of gold does it contain?

12. What weight of chlorauric acid can be prepared from the gold present in a five-dollar gold piece (see preceding problem)?

CHAPTER XLVI

THE STORY OF RADIUM

Introduction. In the spring of 1921 Madame Curie (Fig. 253), professor of physics at the University of Paris, paid a visit to the United States that attracted much attention in the daily press. Many honors were bestowed upon her by universities and scientific societies. By popular subscription the women of our country raised the sum of \$120,000, with which was purchased *one gram* of radium in the form of radium bromide, —the costliest of all materials,—and on their behalf this was presented to Madame Curie by the President of the United States in the White House at Washington. Never before has the visit of a professor from a European country attracted so much attention. Why was this?

Discovery of radium. To answer the question given above we must go back some twenty-six years. In 1895 the German physicist Röntgen discovered a wonderful form of *radiation* capable of passing through glass tubes and acting upon a photographic plate much as light acts. These were the *X rays*, by means of which the surgeon takes pictures of broken bones in the body.

It occurred to the French physicist Becquerel that similar radiations might be given off by those substances that are phosphorescent in the dark. Among others he tried some compounds of the rare metal *uranium*, wrapping them in black paper to exclude light and placing them on a photographic plate. Immediately under these salts the plate was affected as by light, so there *was* a radiation of some kind.

Two facts of great importance were soon discovered: (1) these rays could not pass through metal objects, so that radiographs could be made with them just as with X rays (Fig. 256); (2) when brought near these uranium compounds a charged electroscope was rapidly discharged (Fig. 257), showing that the air all around them was an electrical conductor, which is not true of ordinary air. The property that caused these effects was called *radioactivity*.

Fig. 257 represents a simple form of aluminium-leaf electroscope, the leaves spreading apart (indicated at *B*) when an electric charge is communicated to the knob *A*. When a substance containing uranium (Fig. 258, *C*) is brought near the knob the charge is rapidly lost, and the leaves collapse, as shown at *B*.

Work of the Curies. At the suggestion of Becquerel his associate Pierre Curie and his Polish bride, Madame Curie, took up the problem of radioactivity. They found that *pitchblende*, U_3O_8 (the common ore of uranium), was *four times* as active as pure uranium oxide, and they argued that there must be present in pitchblende a radioactive substance that is not entirely removed in the process of purification. By long-continued work on tons of ore they finally isolated a minute quantity of the chloride of a new element four million times as radioactive as uranium, and which they named *radium*.

In 1906 Monsieur Curie was killed in a street accident, and Madame Curie continued the work, in which many others now engaged. She found the atomic weight of radium to be 226, and this weight, as well as all the properties of the compounds of radium, placed the element in the vacant place below barium in the calcium family. A minute quantity of the metal itself was isolated by Madame Curie in 1910.

Quantity of radium available. In all other instances when a new and very interesting element has been found, energetic search has soon provided a supply. This was not so with radium. It was soon found out that radium occurs in all



FIG. 253. Madame Curie in her laboratory in Paris

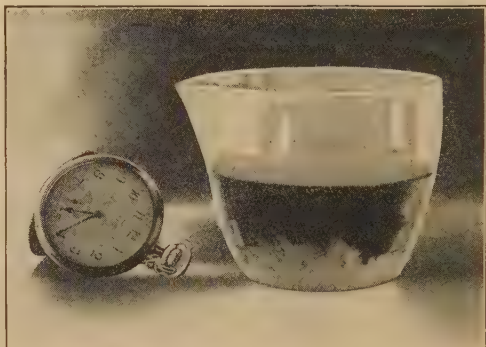


FIG. 254. Picture taken in the laboratory of the Standard Chemical Company, showing the crystallization of the radium bromide which the women of America presented to Madame Curie on the occasion of her visit to America in 1921

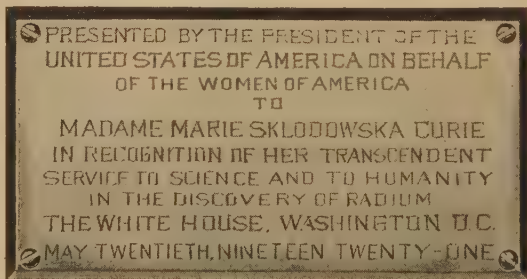


FIG. 255. Inscription on the box containing the radium bromide presented to Madame Curie by the women of America

uranium ores *and in no others*. A still more surprising fact is that in all these ores the *ratio between the uranium and the radium*



FIG. 256. A radiograph of some metal objects

is constant, being about 1 part of radium to 3,200,000 parts of uranium. There is no hope of finding any other ores of radium, and uranium ores themselves are very rare. The older source was

pitchblende, occurring chiefly in Austria. A more abundant source is the rare mineral *carnotite*, found in the deserts of Colorado and Utah.

Up to the present the world's production of radium has been about 160 g. (say 6 oz.), of which the United States has produced about 120 g. In 1920 the production was 35 g. It takes about 500 tons of ore and an equal weight of chemicals to produce *one gram*. The present value is about \$120,000 for every gram of radium content in a salt.

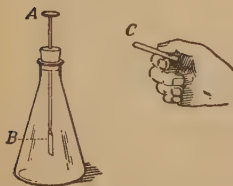


FIG. 258. A discharged electroscopes



FIG. 257. A charged electroscopes

Disintegration of radium. As one looks casually at a sample of a radium salt, such as the chloride, there is little to distinguish it from any other white salt, such as its first cousin, barium chloride. But if we could watch many millions of radium *atoms* we should see a wonderful sight. Every now and then we should see one of these atoms explode violently,

much as now and then a grain of pop corn explodes as we warm the corn, and it then ceases to be a radium atom. The rate at which these explosions take place makes the

average age of a radium atom about twenty-five hundred years. As a result of these explosions all compounds of radium (containing uncounted millions of atoms) are constantly giving off three kinds of so-called rays. These are designated as *alpha rays*, *beta rays*, and *gamma rays*.

A gram of radium shoots off *every second*, at a velocity of 1200 miles per second, 145,000 *billion* particles that are the alpha rays. They consist of positively charged helium atoms. At the same time 71,000 *billion* particles, constituting the beta rays, are shot off, and these have a velocity of about ten times that of the alpha rays. They are negatively charged, and in mass are about $1\frac{1}{845}$ as heavy as hydrogen atoms. They are now called *electrons* and are really *atoms of electricity*. The gamma rays are not made up of matter, but are vibrations in the ether like light. They correspond to the flash of light that often accompanies an ordinary explosion and move with the same velocity as light, but they differ from light in having very short wave-lengths like X rays. The rate of these explosions is kept up very steadily all the time and is not changed by any means as yet tried,—such as very high or very low temperatures,—and all compounds of radium act just alike in the rate of these explosions.

Where radium comes from. Radium is decomposing at a rate that puts its average age at twenty-five hundred years, and yet the rocks in which it is found are very much older than this. Why has any radium survived? Plainly it must be in constant process of formation from some other element, and it has been proved that this parent element is *uranium*. Uranium is also going to pieces (it is radioactive), *but at a much slower rate than radium*. So all uranium ores must contain radium, and none can contain very much. The quantity of radium present is merely the result of equilibrium between the rate of formation and the rate of disintegration. So we see why we shall never find rich radium ores. If anyone were to find such an ore we should have to change all our ideas about radium.

Uranium series of elements. It must not be thought that an atom of radium or of uranium goes entirely to pieces, forming nothing but alpha and beta rays, when it explodes. The loss of a pair of these rays by a uranium atom creates a new atom, which by a fresh explosion gives rise in turn to still another atom. This process continues until, finally, an atom is formed which does not explode, and all radioactivity then ceases. *This final element is lead.* There are in this series thirteen radioactive elements between uranium and lead, radium being the fifth. The immediate product of radium is the gaseous element *niton*, and its explosion is the most terrific of the whole series.

Internal energy of radium. If the explosions of the radium atoms and of the succeeding atoms are as terrific as we have pictured them, and if the alpha and beta rays are shot off with such incredible velocities, the energy set free must be much greater than that of any known reaction between elements. The radium compound actually keeps warm all the time. It is estimated that 1 g. of radium *hourly* evolves 132 cal. of heat and this is kept up for the average life of twenty-five hundred years. From this it can be computed that the total energy given off by a gram of radium in disintegrating into lead is 300,000 times the heat of combustion of a gram of carbon.

Why radium is so important. The way in which the atoms of radium explode, the products formed in the explosion, and the similar conduct of all the elements of the series in which radium has a place make us feel certain that here is a series of elements, of which radium is the best known, whose atoms have an elaborate structure made up of helium atoms and electrons. These must be arranged in such a way as to hold an enormous store of energy — much as a compressed spring holds energy. The very fact that radium resembles the other elements in all ways, apart from radioactivity, and has its natural place in the periodic table makes us suspect that all the other elements have a similar structure, only they explode

so rarely that we never know it. In fact, we now have many other reasons for knowing that this must be the case. It is this revelation as to the nature of atoms that gives to radium its supreme importance as a scientific discovery. The facts seem to indicate that the atoms of all the elements are made up of unit parts and that the nature of these units is the same irrespective of the element.

Practical uses of radium. Such a remarkable material as radium could hardly fail to find useful applications. The rays emitted from radium, niton, and other members of the series, particularly the gamma rays, produce many chemical and physiological effects. They disintegrate glass, water, and many other substances. They render certain materials luminous in the dark, and enamel paints containing radium are used to illumine the hands of watches, the push buttons of electric lights, and the keyholes of doors. They produce severe burns upon the skin like those of X rays. They kill bacteria and other microorganisms.

This latter property has led to the hope that exposure to the radiations of radium compounds might, under proper conditions, prove to be of service in effecting a cure for some diseases of the skin and for cancer. It is not possible to say as yet to what extent these hopes will be realized. Certain forms of cancer have almost certainly been cured in this way, and the progress of other forms has been delayed.

Radioactive thorium. Madame Curie discovered that the rare element *thorium* exhibits properties very similar to those of uranium. It gives rise to a similar series of radioactive elements by successive decomposition, producing the same varieties of radiation as the other series. Uranium and thorium are the elements of greatest atomic weight, and no ordinary elements are known to possess similar properties. This suggests the idea that possibly elements of still higher atomic weight may have existed at some time, but that they have disintegrated into ones of smaller atomic weight which are not radioactive.

The structure of the atom. The facts brought to light in connection with radium prove beyond doubt that each atom is really a complex system, much like a solar system with its sun and planets. The atom of every element contains electrons equal in number to its atomic number (p. 202). The remainder of the atom appears to be composed of helium and hydrogen atoms. Possibly helium atoms are in turn composed of hydrogen. The proofs of these remarkable conclusions belong to advanced courses in physics.

Isotopes. Another conclusion that has been reached in recent years is that the atoms of many of the elements are not all the same in weight, although they have the same chemical properties and cannot be separated by chemical means into collections with different weights. Thus magnesium, with an atomic weight of 24.32, is a mixture of atoms of weights 24, 25, and 26 always in constant ratio and averaging 24.32. Such an element is said to be composed of *isotopes*. Apparently all the atoms have weights that are whole numbers, and all the atoms with fractional atomic weights are mixtures of isotopes.

EXERCISES

1. What is the meaning of the words *alpha*, *beta*, and *gamma*?
2. What is the velocity of light (see physics)?
3. How is an electroscope charged?
4. In what connection has the element thorium been mentioned?
5. One of the radioactive elements discovered by Madame Curie was named *polonium*. Can you suggest a reason for the name?
6. The fastest-moving projectiles from a cannon (the German big berthas that bombarded Paris) move a mile a second. How does the velocity of the alpha ray compare with this?
7. If abundant deposits of uranium ores should be discovered, would radium ever become a cheap element?

CHAPTER XLVII

SOME APPLICATIONS OF RARER ELEMENTS

Rarer elements. A large number of elements are known which have not been described in the foregoing pages because an acquaintance with them is not at all necessary for an understanding of the principles of chemistry. Some of these, while comparatively rare, could be produced in considerable quantities if there were any commercial use for them. A good example is *tellurium*, an element in the sulfur family obtained as a by-product in copper refining. Others are so rare that the cost of production is prohibitive, even though they have very useful properties.

Application in the industries. Some of these less familiar elements or their compounds have properties which make them valuable for special purposes, and mention of a few of these applications will be of interest.

The rare earths constitute a group of about sixteen elements, all resembling aluminium in a general way. They are very difficult to separate from each other and always occur together in nature. Very large quantities of a mixture of them accumulate in the extraction of *thorium* from monazite sand (p. 230). The only one whose compounds are obtained pure rather easily is *cerium*. Compounds of cerium are used as mordants, as catalytic agents, and in medicine and photography. An alloy of cerium with iron is used as a gas or cigar lighter, since it gives off a stream of sparks when scratched by hard iron.

Thorium oxide, mixed with 1 per cent of cerium oxide, constitutes the material of which most gas mantles are made (p. 230).

Zirconium is found in abundance in Brazil in the form of the oxide ZrO_2 . This oxide has an exceedingly high melting point and is made into bricks, and these are used (under the name *zircite*) for lining furnaces.

Titanium in the silicon family is an abundant element, occurring chiefly as the oxide TiO_2 , called *rutile*, and as a constituent of certain iron ores (*ilmenite*). Large quantities of nearly pure titanium or of ferrotitanium are used in making steel rails designed to stand very heavy wear (railway curves and terminals). Titanium oxide is also incorporated in electric-arc carbons (*flaming arc*), which then give a more diffused and efficient light than those made from pure carbon. The oxide is also used to impart a yellow color to porcelain and to artificial teeth.

Vanadium occurs in considerable quantities in carnotite (p. 423) and in certain sulfides found in Peru. Ferrovandium, like ferrotitanium, is used in producing special grades of steel, particularly when great toughness is desired (automobile parts). Its compounds are used as photographic developers, as catalytic reagents in the dye industry (aniline black), as coloring materials in glass, and as mordants.

Molybdenum compounds are used in coloring pottery and in dyeing silk, wool, and leather.

Tungsten compounds are produced in fairly large quantities. It has been found possible to draw the metal into very fine wire (0.3 mm.), which has largely replaced carbon as a filament for electric lamps. Its melting point is very high (3400°), and the consumption of electrical energy for a given candle power is so low that the lamp is about three times as efficient as the older (carbon) lamp. The metal has replaced platinum for electrical contacts

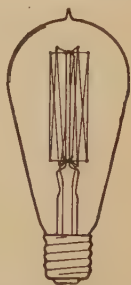


FIG. 259. The ordinary type of tungsten lamp

in switches, telephone jacks, and automobile vibrators. Ferrotungsten is used in making steel designed for lathe tools, since such steel can be heated to a red glow without losing temper.

Uranium oxide is used in making the greenish-yellow glass so familiar in lamp shades, and as a pigment in china glazes.

Selenium, an element in the sulfur family, is obtained as a by-product in refining copper. It is a nonconductor of electricity *when in the dark*, but becomes a fairly good conductor *when exposed to light*. This has led to its use in automatic fire alarms and for regulating automatic gas buoys at sea. Added to glass it produces a fine red color (p. 368), such glass being used for automobile tail-lights and railway lanterns. It is also used to produce red enamels.

Iridium gives a very hard alloy with platinum and is used for pen points, compass bearings, and standard weights and measures.

Palladium is only about half as heavy as platinum, melts much lower, and is harder. It is used as a solder for platinum, for making graduated scales in scientific instruments, and as a substitute for platinum in jewelry. In the form of a powder it is a remarkably active catalytic agent.

APPENDIX

CHEMICAL LIBRARY

Every high school should have at least a few books dealing in a popular way with topics of interest to students beginning chemistry. A large number of such books is available; all are interesting, and some as fascinating as any story of romance ever written. The titles of a few such books are given below. Schools having only a limited sum of money for the purchase of books should select those marked with an asterisk. Prices can be obtained from any bookstore. A great deal of important literature bearing upon chemical topics may be had free of charge. This is true of the bulletins published by certain departments of the Federal government, especially the Department of Agriculture and the Bureau of Standards, Washington, D.C. A list of available bulletins may be obtained by addressing these departments.

Much that is interesting in regard to the subject will be found in the files of various periodicals. Every laboratory should subscribe for *School Science and Mathematics*, published nine times a year by Smith and Turton, Mount Morris, Illinois. *The Independent*, published by the Independent Corporation, New York City, contains occasional articles on chemistry by Edwin Slosson, who is the best of modern writers on popular chemistry. *The Scientific American* also contains numerous articles on chemical topics.

LIST OF SUPPLEMENTARY BOOKS

- ALLYN. Elementary Applied Chemistry. Ginn and Company.
BAILEY. A Textbook of Sanitary and Applied Chemistry. The Macmillan Company.
BANCROFT. Applied Colloid Chemistry. McGraw-Hill Book Company.
BASKERVILLE. Municipal Chemistry. McGraw-Hill Book Company.
BENSON. Industrial Chemistry. The Macmillan Company.

- *BIRD. Modern Science Reader. The Macmillan Company.
- Century Science Series. Separate biographies of Dalton, Davy, Faraday, Liebig, and Pasteur.
- COLLINS. The Wonders of Chemistry. Thomas Y. Crowell Company.
- CUSHMAN. Chemistry and Civilization. Richard G. Badger.
- DAVY. The Elementary Nature of Chlorine. The University of Chicago Press.
- *DUNCAN. The Chemistry of Commerce. Harper & Brothers.
- *DUNCAN. The New Knowledge. Harper & Brothers.
- *DUNCAN. Some Chemical Problems of Today. Harper & Brothers.
- *FARADAY. Chemical History of a Candle. Harper & Brothers.
- FARADAY. The Liquefaction of Gases. The University of Chicago Press.
- *FINDLAY. Chemistry in the Service of Man. Longmans, Green & Co.
- FREAR. Breakfast Foods, *Bulletin 162*, Dairy and Food Division, Department of Agriculture, Harrisburg, Pennsylvania.
- GRANT. Chemistry of Bread-Making. Longmans, Green & Co.
- *GREEN. Coal and Coal Mines. Houghton Mifflin Company.
- HALE. American Chemistry. D. Van Nostrand Company.
- HALLIGAN. Fundamentals of Agriculture. D. C. Heath & Co.
- HARROW. Eminent Chemists of our Time. D. Van Nostrand Company.
- *HART. Leavening Agents. Chemical Publishing Co.
- *HAWK. What we Eat. Harper & Brothers.
- *HENDRICKS. Everyman's Chemistry. Harper & Brothers.
- *JENKS. Chemistry for Young People. Frederick A. Stokes Company.
- JORDON. Principles of Human Nutrition. The Macmillan Company.
- LASSAR-COHN (translated by Muir). Chemistry in Daily Life. H. Grevel Co., London.
- MCPHERSON and HENDERSON. A Course in General Chemistry. Ginn and Company.
- *MARTIN. The Story of a Piece of Coal. George Newnes, Ltd., London.
- *MARTIN. Triumphs and Wonders of Modern Chemistry. D. Van Nostrand Company.
- *MEADE. Story of Gold. D. Appleton and Company.
- MUIR. Heroes of Science — Chemists. E. & J. B. Young & Co.
- *MUIR. The Story of Alchemy. D. Appleton and Company.
- OLSEN. Pure Foods. Ginn and Company.
- PHILIP. Romance of Modern Chemistry. J. B. Lippincott Company.
- *PILCHER and JONES. What Industry owes to Chemical Science. D. Van Nostrand Company.

- *PRIESTLEY. The Discovery of Oxygen. The University of Chicago Press.
- RAMSAY. Gases of the Atmosphere. The Macmillan Company.
- ROSE. Feeding the Family. The Macmillan Company.
- *SCHEELE. The Discovery of Oxygen. The University of Chicago Press.
- SCHEELE. The Early History of Chlorine. The University of Chicago Press.
- Scientific American Cyclopedia of Formulæ. Munn & Company, New York City.
- SHERMAN. Chemistry of Food and Nutrition. The Macmillan Company.
- *SLOSSON. Creative Chemistry. The Century Co.
- SMITH. Chemistry in America. D. Appleton and Company.
- SMITH. Life of Robert Hare. J. B. Lippincott Company.
- *SMITH. Story of Iron. D. Appleton and Company.
- *SNELL. Elementary Household Chemistry. The Macmillan Company.
- *SNYDER. Chemistry of Plant and Animal Life (popular).
- STEWART. Chemistry and its Borderland. Longmans, Green & Co.
- SURFACE. Story of Sugar. D. Appleton and Company.
- *TOWER. Story of Oil. D. Appleton and Company.
- *VENABLE. A Short History of Chemistry. D. C. Heath & Co.
- VULTE and VENDERBILT. Food Industries. Chemical Pub. Co.
- WARDELL and WHITE. A Study of Foods. Ginn and Company.
- WILEY. Foods and their Adulteration. P. Blakiston's Son & Co.
- WOOLMAN and MCGOWAN. Textiles. The Macmillan Company.
- *WOOD. Story of a Loaf of Bread. G. P. Putnam's Sons.
- United States Department of Agriculture: (1) Composition of Foods, *Bulletin 28*, Office of Experiment Stations; (2) Nutritive Value of Foods, *Farmers' Bulletin 142*; (3) Some Forms of Food Adulteration and Simple Methods for their Detection, *Bulletin 100*, Bureau of Chemistry; (4) Industrial Alcohol, *Farmers' Bulletins 268, 269*; (5) Household Tests for the Detection of Oleomargarine and Renovated Butter, *Farmers' Bulletin 363*; (7) Canned Fruits, Preserves, and Jellies, *Farmers' Bulletin 203*. (Send to the Department of Agriculture, Washington, D. C., for list of available bulletins and select such as may be of interest.) (8) Removal of Stains from Clothing and other Textiles, *Farmers' Bulletin 861*.
- United States Bureau of Standards: Measurements in the Home, *Circular 55*; Common Materials used in the Home, *Circular 70*; Problem of Safety, *Circular 75*; Inks, *Circular 95*.

THERMOMETERS

A thermometer is the well-known instrument used for measuring temperatures. It consists of a glass bulb joined to a thick-walled glass tube which has a very small but uniform bore (Fig. 260). There are two kinds of thermometers in common use: the Fahrenheit (F.), ordinarily used in our homes, and the centigrade (C.), used for all scientific purposes. These differ only in the manner in which they are graduated. In their construction the bulb and tube are filled with mercury, and the bulb is then



FIG. 260. The centigrade and Fahrenheit scales

surrounded by melting ice. The mercury contracts as it reaches the temperature of the melting ice and remains stationary when this temperature is reached. The height of the mercury in the tube is then marked on the tube. The thermometer is next immersed in boiling water or steam (under a pressure of 1 atmosphere). The height to which the mercury rises is again marked on the tube. In the Fahrenheit thermometer the melting point of ice and the boiling point of water are marked 32° and 212° respectively, and the space between these two points on the tube is divided into 180 equal parts (degrees); in the centigrade thermometer the two points noted above are marked 0° and 100° respectively, and the intervening space on the thermometer tube divided into 100 equal parts (Fig. 260). In other words, in the Fahrenheit system ice melts at 32° and water boils at 212°, while in the centigrade ice melts at 0°

and water boils at 100°. In the construction of thermometers the divisions on the tube may be extended below the melting point of ice and above the boiling point of water and, of course, must be of the same length.

It is easily possible to convert readings on the Fahrenheit scale into the corresponding readings on the centigrade scale and vice versa. It is only necessary to keep in mind that 180° on the Fahrenheit scale (the difference in degrees between the melting

point of ice and the boiling point of water) equals 100° on the centigrade (or 1° F. equals $\frac{5}{9}^{\circ}$ C.) and that 32° F. is the same as 0° C. The above relations are expressed in the following equation:

$$\frac{C}{F - 32} = \frac{5}{9}$$

Suppose we wish to convert 75° F. into centigrade reading: substituting 75 for F in the above equation, we have

$$\frac{C}{75 - 32} = \frac{5}{9}$$

Solving for C , we have

$$9 C = 5 (75 - 32)$$

$$9 C = 215$$

$$C = 23.8^{\circ} \text{ F.}$$

Similarly, if we wish to convert centigrade readings into Fahrenheit we substitute the centigrade reading for C in the above equations and solve for F .

DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS

NAME	DENSITY	MELTING POINT	NAME	DENSITY	MELTING POINT
Aluminium	2.65	658.7°	Manganese	8.01	1230.0°
Antimony	6.70	630.0°	Mercury	13.56	-38.87°
Arsenic	5.73	—	Nickel	8.90	1452.0°
Bismuth	9.80	271.0°	Phosphorus	1.83	44.0°
Calcium	1.55	810.0°	Platinum	21.50	1755.0°
Carbon (diamond)	3.52	—	Potassium	0.862	62.3°
Carbon (graphite)	2.30	3600.0°	Radium	—	700.0°
Chromium	7.30	1615.0°	Silicon	2.35	1420.0°
Cobalt	8.60	1480.0°	Silver	10.50	960.5°
Copper	8.93	1083.0°	Sodium	0.97	97.5°
Gold	19.32	1063.0°	Sulfur (rhombic)	2.06	112.8°
Iron	7.86	1530.0°	Tin	7.30	231.9°
Lead	11.37	327.4°	Zinc	7.10	419.4°
Magnesium	1.74	651.0°			

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 CC. OF WATER AT		
		0°	20°	100°
Calcium chloride . .	CaCl ₂	59.5 g.	74.5 g.	159.0 g.
Sodium chloride . . .	NaCl	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate . .	KNO ₃	13.30 g.	31.6 g.	246.0 g.
Copper sulfate . . .	CuSO ₄	14.30 g.	20.7 g.	75.4 g.
Calcium sulfate . . .	CaSO ₄	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide . .	Ca(OH) ₂	0.185 g.	0.165 g.	0.077 g.

TENSION OF AQUEOUS VAPOR EXPRESSED IN MILLIMETERS OF MERCURY

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
15°	12.78	21°	18.62
16°	13.62	22°	19.79
17°	14.52	23°	21.02
18°	15.46	24°	22.32
19°	16.56	25°	23.69
20°	17.51	100°	760.00

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EXAMINATION QUESTIONS

The following are typical questions selected from the examinations given in chemistry by the College Entrance Examination Board.

1. Define the terms *molecule*, *atom*, and *ion*.
2. State Avogadro's hypothesis and show how it guides the chemist in determining molecular weights.
3. (a) What takes place when steam is passed over heated zinc or iron? (b) How would you identify the products? (c) What do you learn about the composition of water from this experiment?
4. Outline three different methods for obtaining oxygen. Give some idea of their relative cost.
5. Distinguish between a chemical law and a chemical theory.
6. Name three laws dealing with weights; three dealing with gases.
7. Name two important theories in chemistry.
8. Why does wood burn with a flame while charcoal merely glows?
9. Can you light a jet of oxygen in an atmosphere of (a) air? (b) of hydrogen? Explain.
10. State the law of multiple proportions. Give two substances to illustrate the law, with the percentage composition in each case.
11. (a) What is a saturated solution of a solid in a liquid? (b) How does increasing the temperature affect the solubility of solids in liquids? (c) In what two ways could a saturated solution of sodium chloride in water be prepared? How could you satisfy yourself that the solution is just saturated in both cases?
12. (a) Name two elements which are liquid at ordinary temperatures. (b) Name the common allotropic forms of each of four elements. (c) Name two elements having exceptionally high melting points, and state how this property is put to practical use in the case of each.
13. (a) Describe briefly an experiment to determine the percentage of oxygen in air. (b) State fully the composition of air. (c) How are the freezing point and the boiling point of a solvent affected by dissolved substances? Give a practical application of one of these facts.
14. (a) Distinguish between chemically pure water and spring water. (b) How may water be purified on a small scale for household use? How is it purified on a large scale for a city supply? (c) Name one impurity which

renders water unfit for use in laundries and outline a practical method for removing it.

15. Define and give an example of (a) catalysis, (b) equivalent of an element, (c) allotropy, (d) molecular weight, (e) carbohydrate.

16. (a) What is a reversible reaction? Illustrate by means of an equation. (b) Under what three conditions will a reaction go to completion? (c) On the basis of the electrolytic dissociation theory, how would you explain (1) the neutralization of an acid by a base? (2) the changes that take place when a solution of copper sulfate is electrolyzed between copper electrodes?

17. (a) State the physical and chemical characteristics of chlorine, bromine, and iodine as regards physical state, color, solubility, tendency to combine with hydrogen. (b) How may bleaching powder be made? What are its properties?

18. Given the valence of A as 3, derive the probable valence of B, C, and D from the following formulas: A_2B_3 , B_2C , B_5D_2 . What would be the formula of a compound of A with C?

19. Write equations for the following reactions, using formulas throughout (to receive credit the equations must be absolutely correct):

- a. Sodium acid carbonate + sulfuric acid =
- b. Carbon dioxide + heated carbon =
- c. Silver sulfate + barium chloride =
- d. Copper + hot concentrated sulfuric acid =
- e. Hydrogen sulfide burned in excess of air =
- f. Potassium chlorate heated with manganese dioxide =

20. How should you proceed to produce the first-mentioned substance from the second in four of the following cases? Describe each step in the process. (a) Nitrogen from the atmosphere; (b) kerosene from crude petroleum; (c) sulfuric acid from sulfur; (d) limewater from marble; (e) hydrochloric acid from sulfuric acid.

21. (a) What is meant by the relative activity of the metallic elements? (b) Arrange in order of decreasing activity the following: gold, hydrogen, zinc, sodium, copper (the arrangement must be correct throughout to receive credit).

22. Answer four of the following questions: (a) Explain the cleansing action of soaps. Of what substances are washing powders likely to be composed? (b) Describe one method of converting pig iron into steel. (c) Explain upon a chemical basis the use of ozone in the purification of water. (d) Name two products of commercial importance that can be obtained by chemical change from starch. (e) What rôle does each of the three general classes of foods play in nutrition?

23. Mention very briefly *any* means of identifying with certainty each of the following gases: hydrogen, nitrogen, carbon dioxide, sulfur dioxide, nitrous oxide, chlorine, carbon monoxide, hydrogen sulfide, oxygen, ozone.

24. Which contains the more energy under the same conditions of temperature and pressure: a mixture of 1 g. of hydrogen and 8 g. of oxygen or 9 g. of water? Give the reason for your conclusion.

25. (a) Why is sulfuric rather than hydrochloric acid used in making acids? (b) Why is hydrochloric rather than nitric acid used in making hydrogen sulfide? (c) Why is hydrochloric rather than sulfuric acid used in making carbon dioxide from marble? (d) Why is sulfuric rather than hydrochloric acid used in preparing oxygen from water by electrolysis? (e) Why is nitric rather than hydrochloric acid used to dissolve a silver coin? (f) Why is dilute rather than concentrated sulfuric acid used in making hydrogen?

26. (a) How many cubic centimeters of oxygen, measured at 0°C . and 760 mm., can be obtained by the complete decomposition of 1 kg. of 3 per cent solution of hydrogen peroxide, H_2O_2 , into water and oxygen? (H 1, O 16.) (Note: A liter of oxygen at 0° and 760 mm. weighs 1.43 g.) (b) What is the percentage of silica, SiO_2 , in the mineral analcite, $\text{Na}_2\text{SiO}_3 \cdot \text{Al}_2(\text{SiO}_3)_3 \cdot 2\text{H}_2\text{O}$? (Si 28, Al 27, Na 23, O 16, H 1.)

27. How many grams of water of crystallization are there in the crystallized barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, obtained from 10 g. of barium? (Atomic weights: Ba 137, Cl 35.5, O 16, H 1.)

28. Ten liters of a gas whose formula is $\text{C}_2\text{H}_6\text{O}$ are completely burned in oxygen. How many liters of oxygen gas are required for its complete combustion? How many liters of carbon dioxide should result? All volumes are measured under the same conditions of temperature and pressure.

29. If 50.0 g. of calcium carbonate, CaCO_3 , are added to 50.0 g. of hydrochloric acid, HCl , in water solution, which substance remains in excess? What is the weight of this excess? (Atomic weights: Ca 40, Cl 35.5, O 16, C 12, H 1.)

30. (a) State Gay-Lussac's law of combining volumes. What volume of oxygen is required for the complete combustion of 5 liters of acetylene, C_2H_2 ? All measurements are to be made under the same conditions of temperature and pressure. (b) One liter of gas A weighs 1.98 g. One liter of gas B weighs 0.77 g., under the same conditions. The molecular weight of A is 44. What is the molecular weight of B?

31. How many grams of sodium hydroxide will be required to neutralize 9.8 g. of sulfuric acid? Name the products formed and determine the weight of each product. (Atomic weights: H 1, O 16, Na 23, S 32.)

32. A certain chemical compound is found by analysis to contain 92.3 per cent of carbon and 7.7 per cent of hydrogen. What is the simplest formula which can express its composition? If the molecular weight is 78, what is the formula? (C = 12, H = 1.)

LIST OF THE ELEMENTS, THEIR SYMBOLS AND THEIR ATOMIC WEIGHTS

The more important elements are printed in heavier type

O = 16

Aluminium Al	27.10	Molybdenum Mo	96.00
Antimony Sb	120.20	Neodymium Nd	144.30
Argon A	39.90	Neon Ne	20.20
Arsenic As	74.96	Nickel Ni	58.68
Barium Ba	137.37	Niton Nt	222.40
Bismuth Bi	208.00	Nitrogen N	14.008
Boron B	10.90	Osmium Os	190.90
Bromine Br	79.92	Oxygen O	16.00
Cadmium Cd	112.40	Palladium Pd	106.70
Cæsium Cs	132.81	Phosphorus P	31.04
Calcium Ca	40.07	Platinum Pt	195.20
Carbon C	12.005	Potassium K	39.10
Cerium Ce	140.25	Praseodymium Pr	140.90
Chlorine Cl	35.46	Radium Ra	226.00
Chromium Cr	52.00	Rhodium Rh	102.90
Cobalt Co	58.97	Rubidium Rb	85.45
Columbium Cb	93.10	Ruthenium Ru	101.70
Copper Cu	63.57	Samarium Sa	150.40
Dysprosium Dy	162.50	Scandium Sc	44.10
Erbium Er	167.70	Selenium Se	79.20
Europium Eu	152.00	Silicon Si	28.30
Fluorine F	19.00	Silver Ag	107.88
Gadolinium Gd	157.30	Sodium Na	23.00
Gallium Ga	70.10	Strontium Sr	87.63
Germanium Ge	72.50	Sulfur S	32.06
Glucinum Gl	9.10	Tantalum Ta	181.50
Gold Au	197.20	Tellurium Te	127.50
Helium He	4.00	Terbium Tb	159.20
Holmium Ho	163.50	Thallium Tl	204.00
Hydrogen H	1.008	Thorium Th	232.15
Indium In	114.80	Thulium Tm	168.50
Iodine I	126.92	Tin Sn	118.70
Iridium Ir	193.10	Titanium Ti	48.10
Iron Fe	55.84	Tungsten W	184.00
Krypton Kr	82.92	Uranium U	238.20
Lanthanum La	139.00	Vanadium V	51.00
Lead Pb	207.20	Xenon Xe	130.20
Lithium Li	6.94	Ytterbium Yb	173.50
Lutecium Lu	175.00	Yttrium Yt	89.30
Magnesium Mg	24.32	Zinc Zn	65.37
Manganese Mn	54.93	Zirconium Zr	90.60
Mercury Hg	200.60		

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STAND-
ARD CONDITIONS AND BOILING POINTS UNDER PRESSURE OF
760 MILLIMETERS

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene . . .	1.1621	-83.8°	Hydrogen chloride	1.6398	-83.1°
Air	1.2928		Hydrogen fluoride	0.893	+19.4°
Ammonia . . .	0.7708	-33.5°	Hydrogen sulfide	1.5392	-61.6°
Argon	1.7809	-186.0°	Methane	0.7168	-164.0°
Carbon dioxide .	1.9768	-78.2°	Nitric oxide . .	1.3402	-153.0°
Carbon monoxide	1.2504	-190.0°	Nitrogen	1.2507	-195.7°
Chlorine	3.1674	-33.6°	Nitrous oxide . .	1.9777	-89.8°
Helium	0.1782	-268.7°	Oxygen	1.4290	-183.0°
Hydrogen	0.08987	-252.7°	Sulfur dioxide .	2.9266	-8.0°

DISPLACEMENT (ELECTROCHEMICAL) SERIES

1. Potassium	7. Manganese	13. Tin	19. Antimony
2. Sodium	8. Zinc	14. Lead	20. Mercury
3. Lithium	9. Chromium	15. Hydrogen	21. Silver
4. Calcium	10. Iron	16. Copper	22. Platinum
5. Magnesium	11. Cobalt	17. Arsenic	23. Gold
6. Aluminium	12. Nickel	18. Bismuth	

RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 pound (troy) = 373.24 grams
1 ounce (troy) = 31.10348 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.3495 grams
1 kilogram = 2.67923 pounds (troy)
1 kilogram = 2.20462 pounds (avoirdupois)
1 liter = 1.05668 United States quarts
1 gallon = 3.78543 liters
1 cubic centimeter = 0.0610 cubic inch
1 cubic inch = 16.3872 cubic centimeters
1 cubic foot = 28,320 cubic centimeters
1 centimeter = 0.3937 inch
1 meter = 39.37 inches

One cubic centimeter of water at its temperature of greatest density (4° C.) weighs approximately 1 g. For all practical purposes, therefore, 1 cc. of water may be regarded as weighing 1 g.



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